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13. ABSTRACT *(Maximum 200 words)*
At the Contemporary Energetics Conference at The MITRE Corporation, McLean, VA on July 20, 2003. In this talk I summarized our DARPA/AFOSR and published Russian efforts to prepare DTTO, IsoDTTO and other energetics. In the present set of overheads I have added further routes (overheads 35, 43, 46 and 50-59) to be investigated for synthesis of various 1,2,3,4-tetrazine, 1,3-di-N-oxides, DTTO, and IsoDTTO. Synthesis of triazolotetrazine dioxides (overhead 35) is now being emphasized. There are notes and explanations on almost all of the overheads to make them more understandable. Such additions were suggested at our June meeting, 2004. I believe that the additions make our work and my talk much more intelligible. In the present overheads our studies of synthesis of 1-nitroacetylenes and dinitroacetylene as sponsored by DARPA/AFOSR have not been included.

14. SUBJECT TERMS

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17. SECURITY CLASSIFICATION OF REPORT

18. SECURITY CLASSIFICATION OF THIS PAGE

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

Synthesis of 1,2,3,4-Tetrazines, 1,2,3,4-Tetrazine Di-N-oxides, Pentazole Derivatives, Pentazine Poly-N-oxides, and Nitroacetylenes

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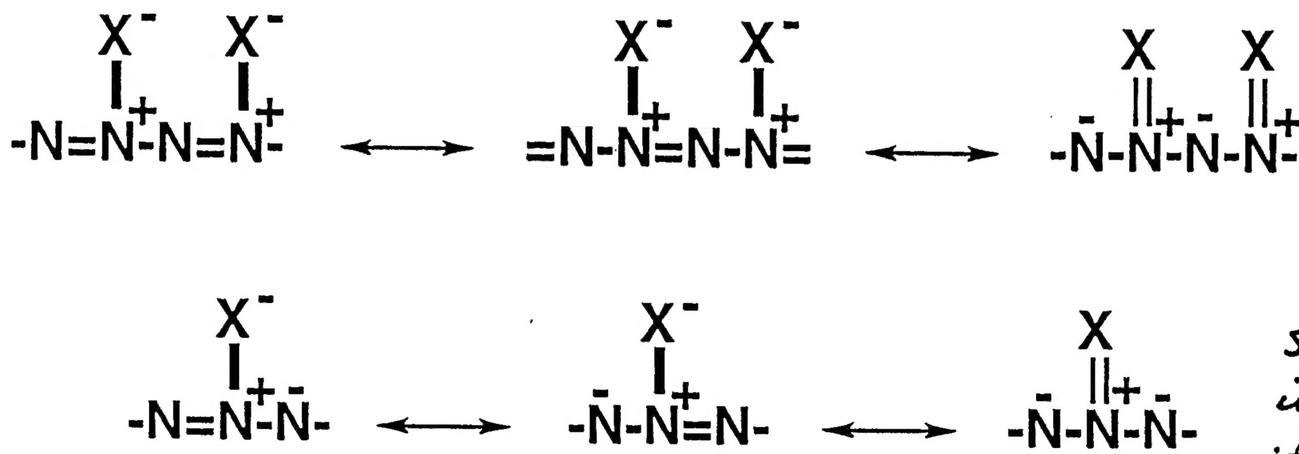
Department of Chemistry, The Ohio State University

Columbus, Ohio

This presentation will be primarily a review of research on the chemistry of 1,2,3,4-tetrazines and 1,2,3,4-tetrazine di-N-oxides as published from Moscow since 1988 by many chemists in the Zelinsky Institute and as explored by Dr. Venugopal at OSU since early 2001. In this talk many new and interesting structures will be considered and if time permits, many approaches to synthesis of energetic molecules will be proposed.

Stabilized Systems
Alternate Positive-Negative Charges (APNC)



This is truly an important concept in considering new syntheses of high-energy materials!

Substitute N for O in nitrate (NO_3^-), nitrite (NO_2^-), pernitrate ($\bar{O}$-O-NO_2) and related oxygen-nitrogen compounds! (R-NO_2, RONO, $RONO_2$, etc)

X = O, NR, and CR_2

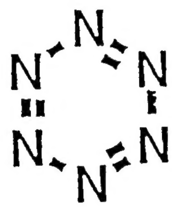
This concept should be made clear to every student of beginning chemistry.

This concept should be extended to boron and phosphorous compounds!

Menkin, 1988; Churakov, 1991

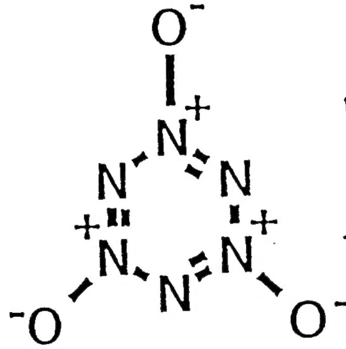
The concept of APNC was originated by Menkin*, a theoretician in Russia, and serves as the basis for my presentation today. The ideas will be extended to many new energetic molecules as yet unknown.

Stabilized N-Oxides



unstable

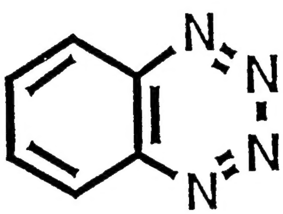
Many chemists in the 1940s tried to prepare N_6, a benzene analog.



life: < 1 sec

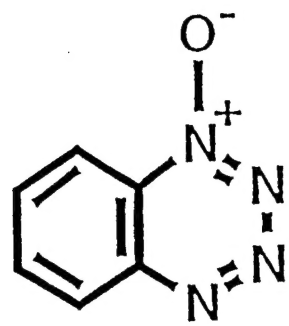
very few chemists know that this molecule, N_6O_3, will go through a mass spectrometer. This molecule is a trimer of nitrous oxide, N_2O

his molecule has ot been generated eviously at low mperature. Is it ble? Can it be pared and ed?



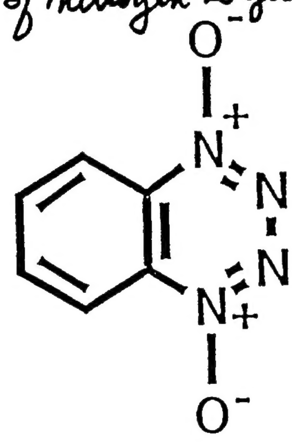
unstable

This molecule undergoes loss of nitrogen to give benzyne!



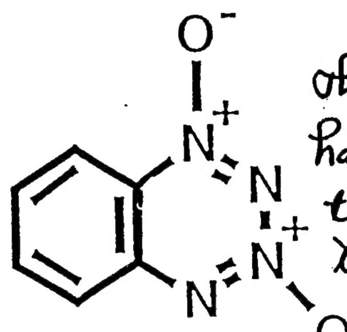
preparable

This tetrazine N-oxide melts at 72-74°C and can be "kept" for 6-7 hours before decomposition.



unstable

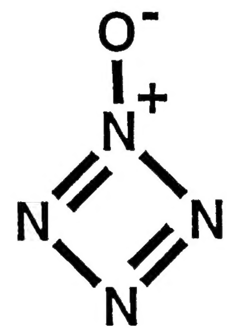
This tetrazine dioxide loses N_2 to form o-dinitrosobenzene. No one has examined this molecule at low temperatures.



stable, usable

The Zelinski chemists have been studying this molecule since the early 1990s or even earlier. well over 30 Russian have been studying this molecule!!

This molecule is stable, now readily prepared, and melts at 172-174°C.



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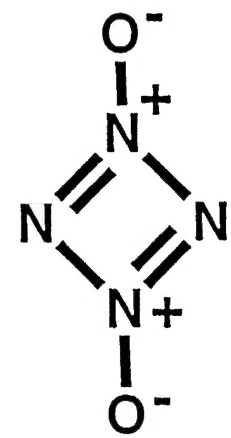

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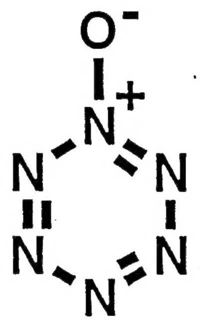

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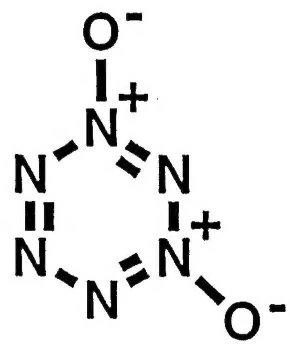

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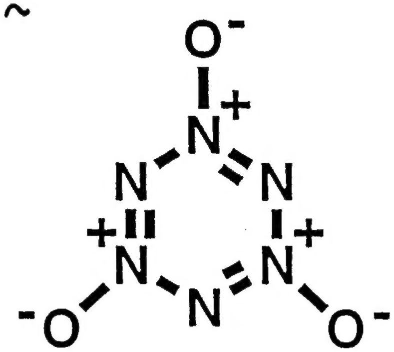

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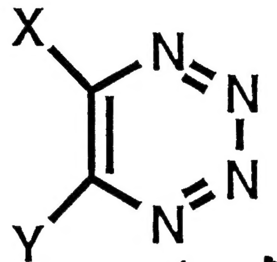
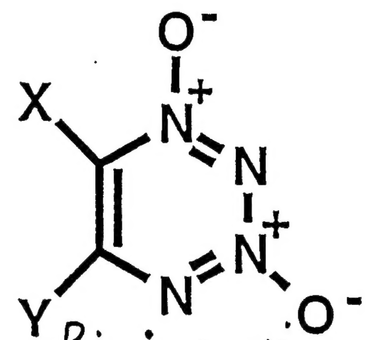
Bartlett et al, *J. Phys. Chem.*, 2001

Prof. Bartlett visited OSU and was informed of the APNC concept. He and his colleagues have calculated that 2 is more stable than 1 and 5 is more stable than 3 and 4. As yet 2 has not been prepared.

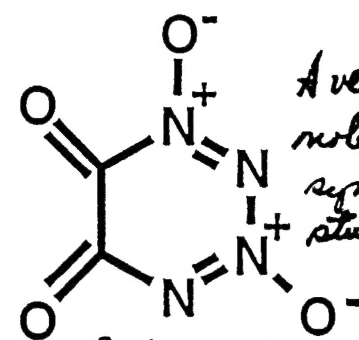
Synthesis of High-Energy Heterocycles



We at OSU are studying preparation, stability, and utility of 1,2,3,4-tetrazines at low temperatures. If such tetrazines can be utilized, this whole area will become very important and economical.

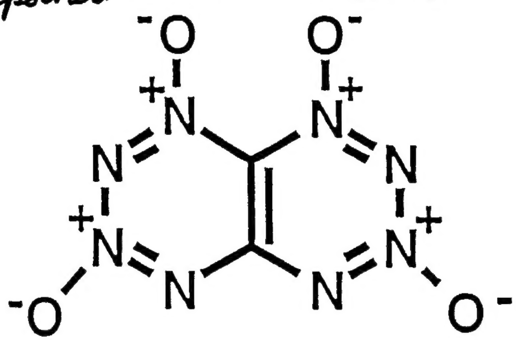


This is a major objective of the program at OSU! Very important.

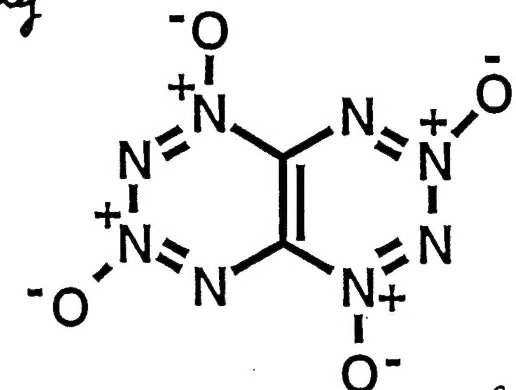


A very important molecule whose synthesis is being studied at OSU! This molecule should be an excellent source of N_2O for use in engines and combustion machines.

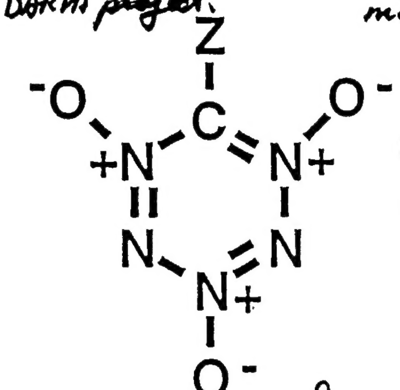
We are beginning study of synthesis of this molecule at OSU on our DARPA project.



DTTO: An enormously important molecule. Synthesis of DTTO is the major objective of the OSU-DARPA-Air Research effort. This molecule is truly important! The Russians are keeping their studies secret !!!



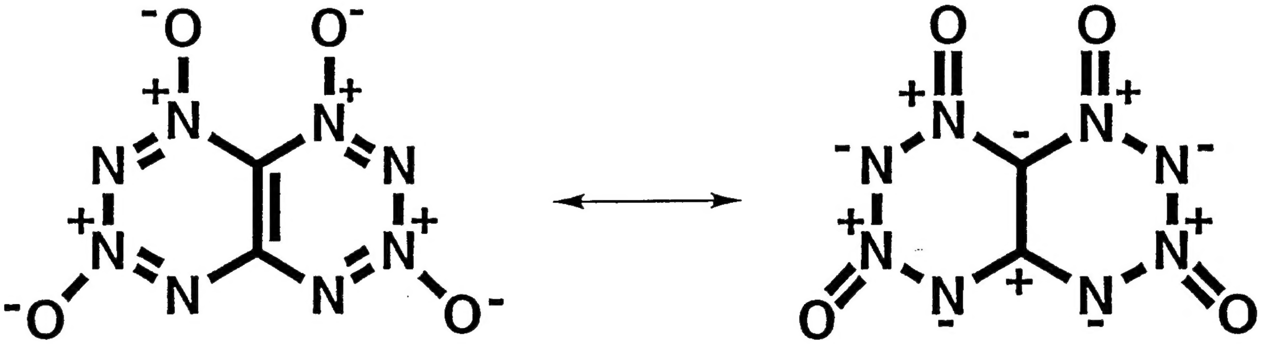
IsoDTTO: an enormously important molecule also being studied in Russia. A major objective of the program by DARPA/AIR FORCE at OSU. See calculations in a later slide.



Calculations are in progress!

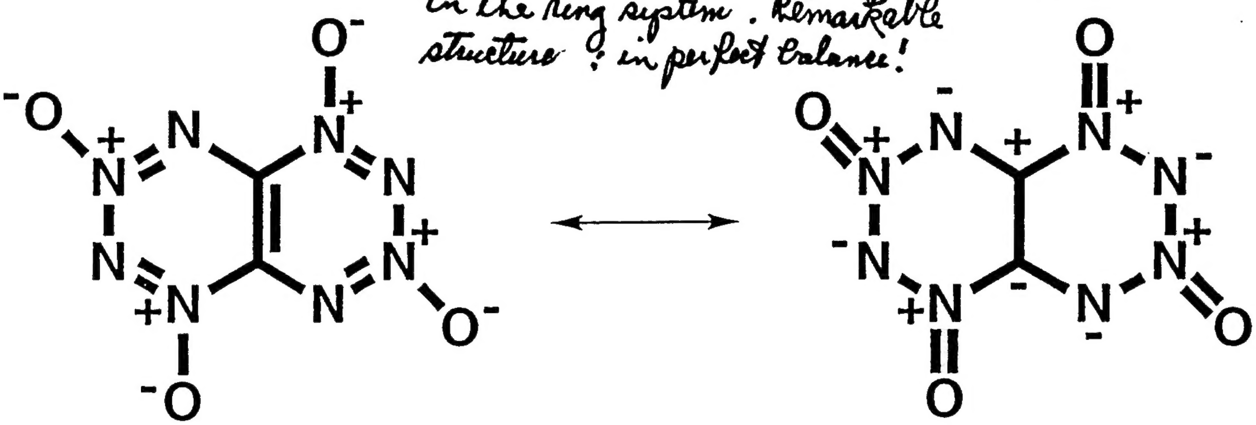
This is an unknown molecule at present. We wish to study its synthesis at OSU. Additional funding will be necessary if study of this molecule is to be emphasized.

The research of Dr. Venugopal at OSU is totally dedicated to practical synthesis of DTTO or/and IsoDTTO. This project needs additional funding if Dr. Venugopal is to stay at OSU and complete this effort



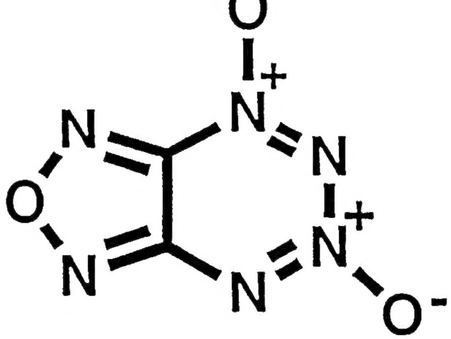
DTTO
(the better molecule)

notice the alternating positive + negative charges in the ring system! Remarkable structure ! in perfect balance!



IsoDTTO

This slide illustrates the APNC characters of DTTO and IsoDTTO. The alternating positive and negative charges in the ring systems are illustrated. Tartakovski emphasized this concept in his West Coast seminar in 1995. We should learn where the Russians and the Chinese are in syntheses of DTTO and IsoDTTO. Are these molecules going to be practical?



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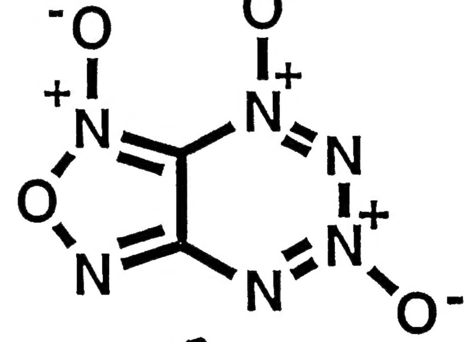

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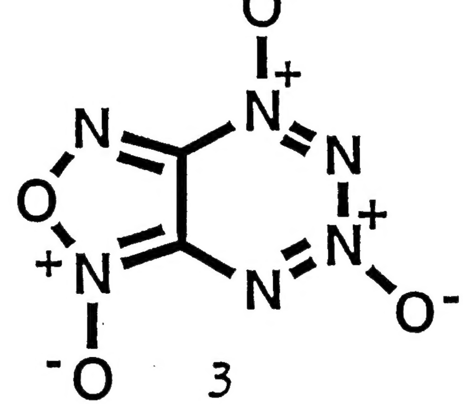

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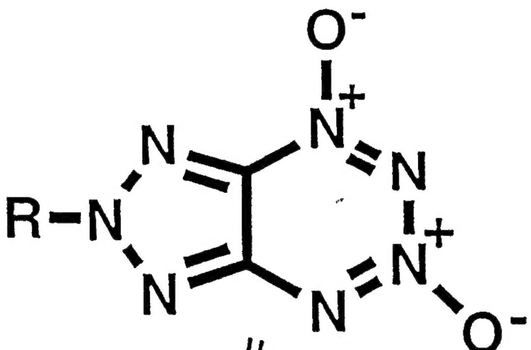

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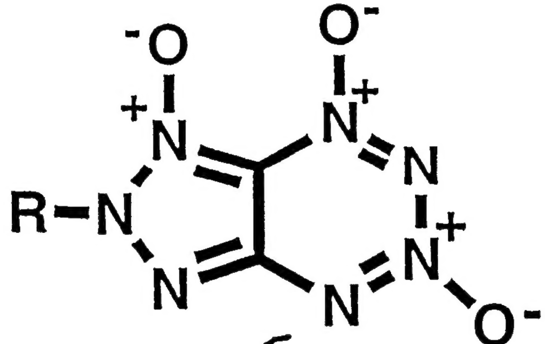

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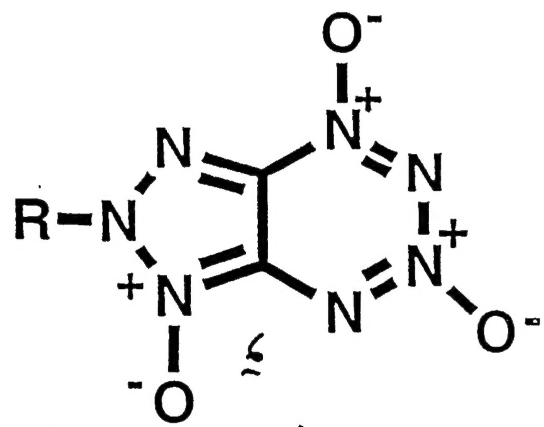

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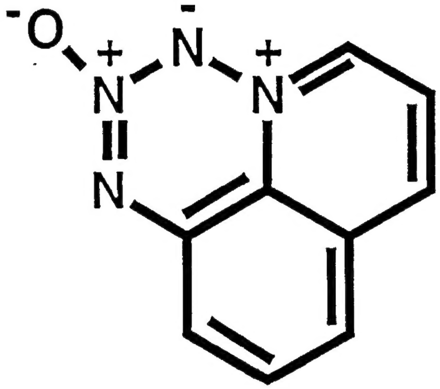
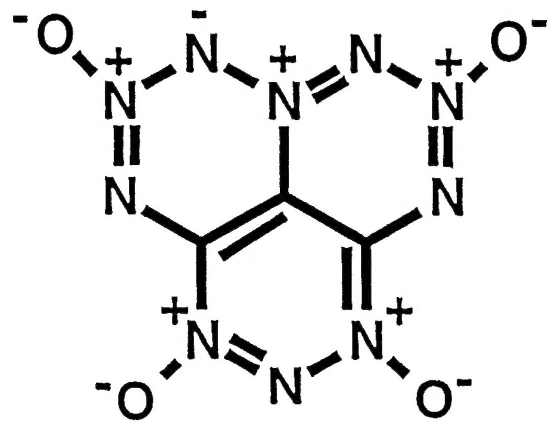
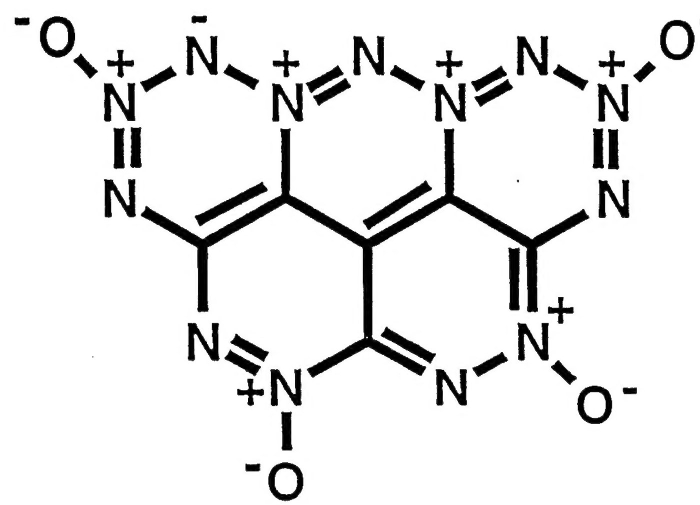
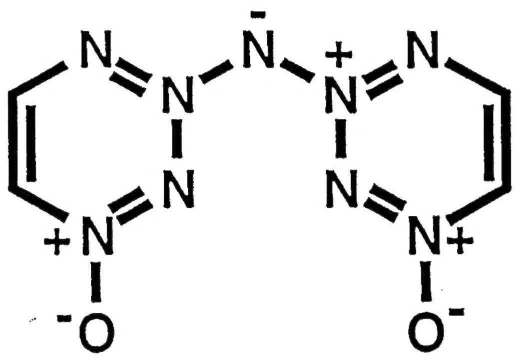
Compound 1 has been synthesized in Moscow and at OSU. It is hoped to convert 1 to 2 or/and 3. As yet this effort has not been successful. Cmpds 2 and 3 are isomers of DTTO and IsoDTTO. At present we do not have good crystals of 1. We want an X-ray analysis of 1 (furazano tetrazine 1,3-di-N-oxide). Identifying the structures of the hydrolysis products of 1 will take time. Study has been initiated of study of synthesis of 4. This study needs further funding.

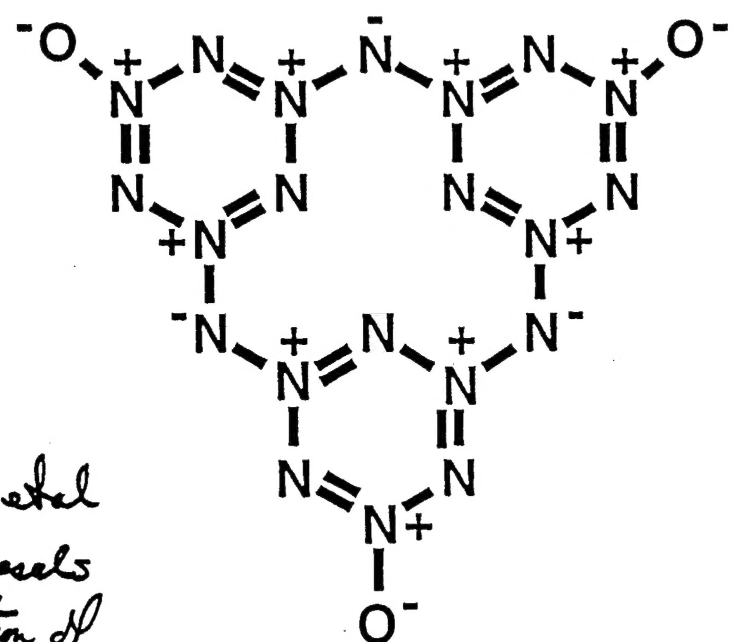
Alternating Positive-Negative Heterocycles





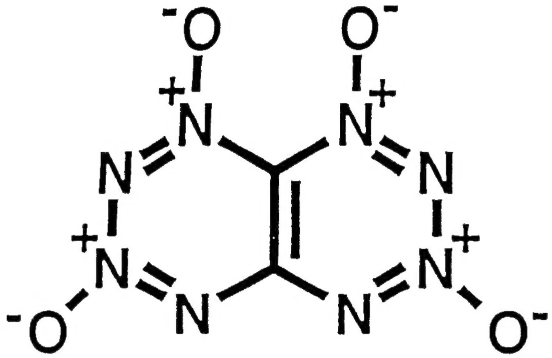






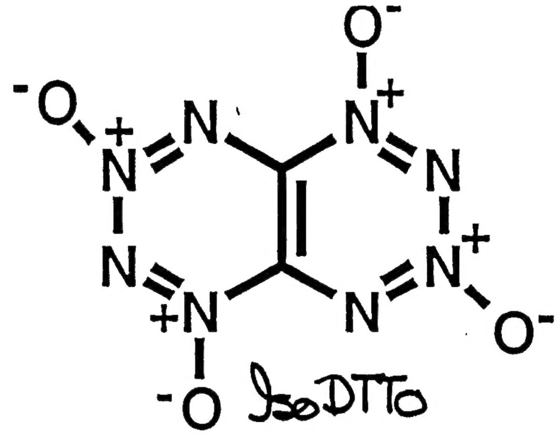
($N_{21}O_3{}^{3+}$)

These molecules have been theorized by Harkin et al to be stable! These molecules lead to proposals of study of polymerization and copolymerization of N_2O and azides (ZN_3). Chemists should really study fixation of N_2O and ZN_3! Later slides will amplify such studies!



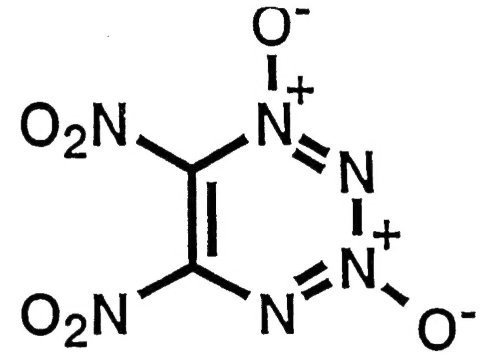
DTTO

$\rho = 2.419\ g\ cm^{-3}$
$\Delta H_f = 179.5\ kcal\ mol^{-1}$
$P_{CJ} = 131.4\ GP_a$



IsoDTTO

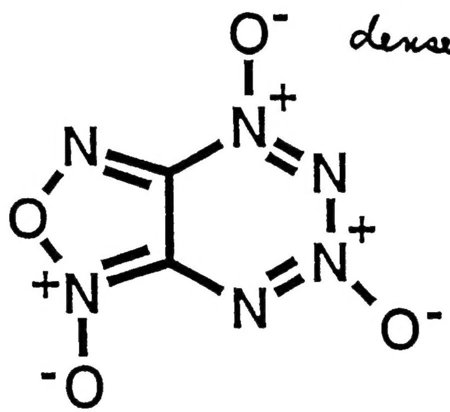
$\rho = 2.484\ g\ cm^{-3}$
$\Delta H_f = 175.7\ kcal\ mol^{-1}$
$P_{CJ} = 131.8\ GP_a$



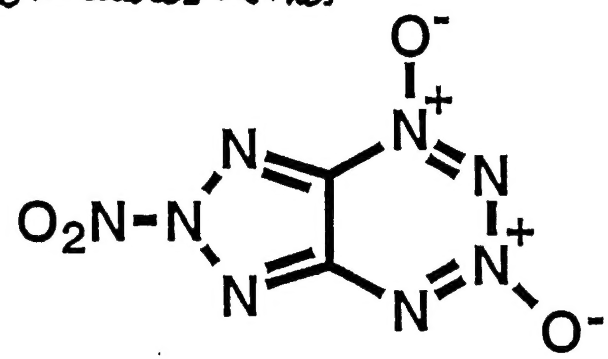
Is such a monocyclic compound stable or practical?!

$\rho = 2.072\ g\ cm^{-3}$
$\Delta H_f = 134.3\ kcal\ mol^{-1}$
$P_{CJ} = 50.6\ GP_a$

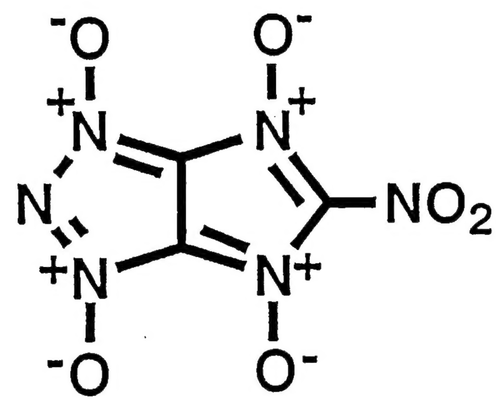
will these molecules be this dense?



$\rho = 2.191\ g\ cm^{-3}$
$\Delta H_f = 128.6\ kcal\ mol^{-1}$
$P_{CJ} = 61.8\ GP_a$

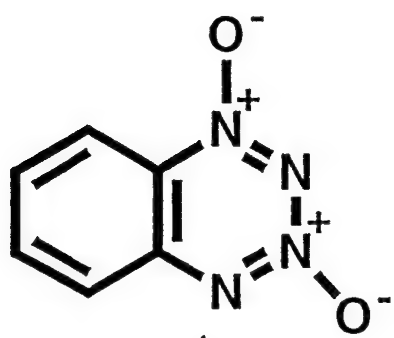


$\rho = 2.179\ g\ cm^{-3}$
$\Delta H_f = 158.1\ kcal\ mol^{-1}$
$P_{CJ} = 61.96\ GP_a$



$\rho = 2.191\ g\ cm^{-3}$
$\Delta H_f = 128.6\ kcal\ mol^{-1}$
$P_{CJ} = 61.8\ GP_a$

These calculations were made by H. Ammon at the Univ. of Maryland. DTTO and IsoDTTO are spectacular!



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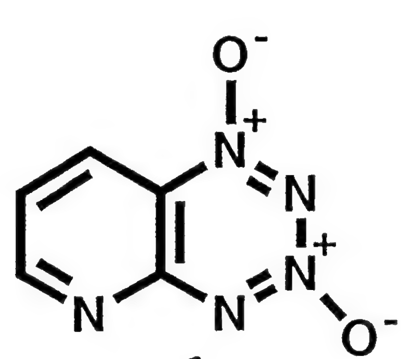

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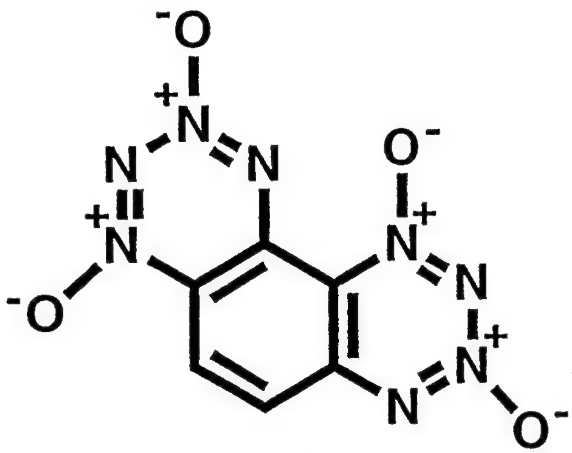

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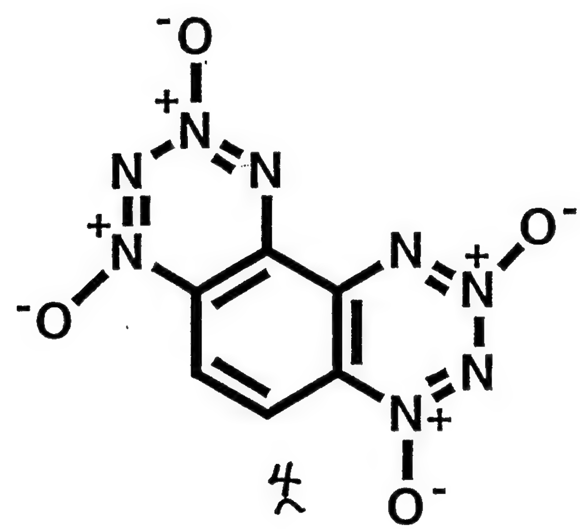

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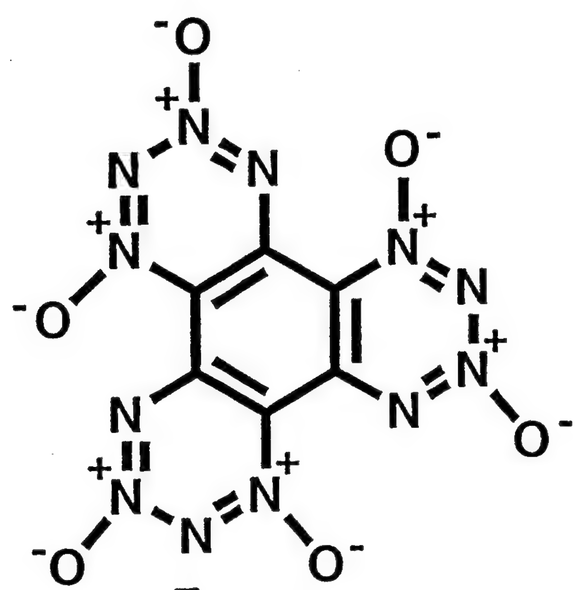

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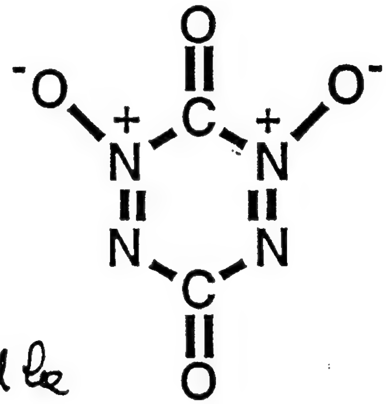
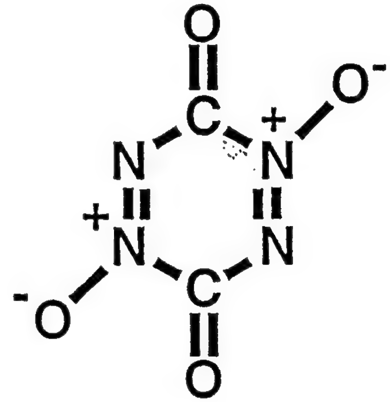
Compounds 1, 2, and 3 have been synthesized in Moscow. They are quite stable. We are sure that preparation of 5 is being attempted by Zelinsky chemists.

Carbon Monoxide-Nitrous Oxide Heterocycles



1



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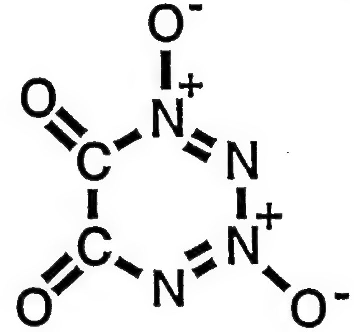

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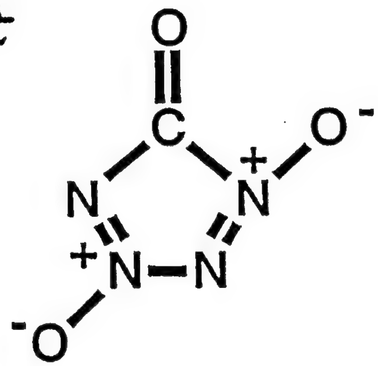
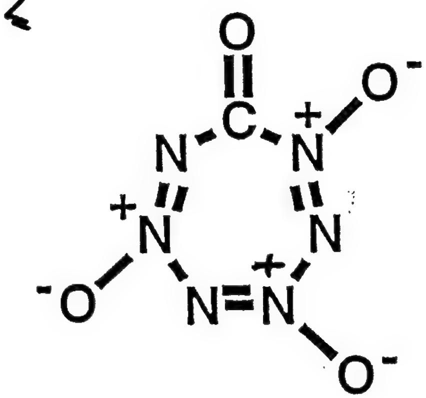
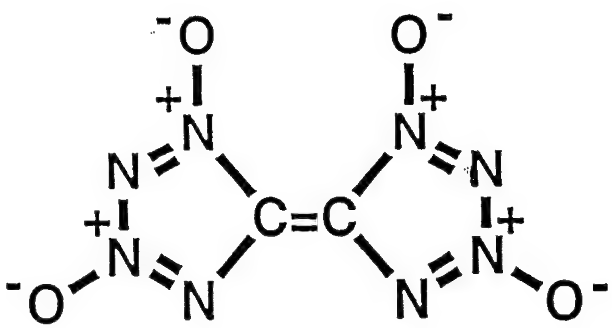
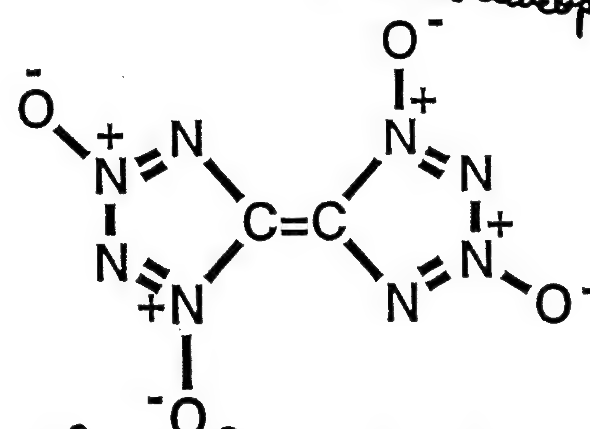
1 and 2 should be practical molecules preparable from phosgene [$COCl_2$] and hydrazine or phosgene and NaN_2ONa!! Important ideas!



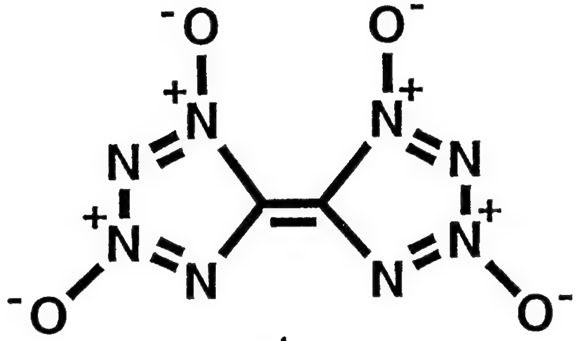


Syntheses of 1 - 3 should be made major efforts!! These molecules also lead to study of the chemistry of NPO, PNO, BNO, and NBO!! These ideas will be developed further at OSU.





These are all new compounds being proposed by OSU for study. They are in perfect CO_2 and N_2 balance - - - and may be valuable as gasoline additives.



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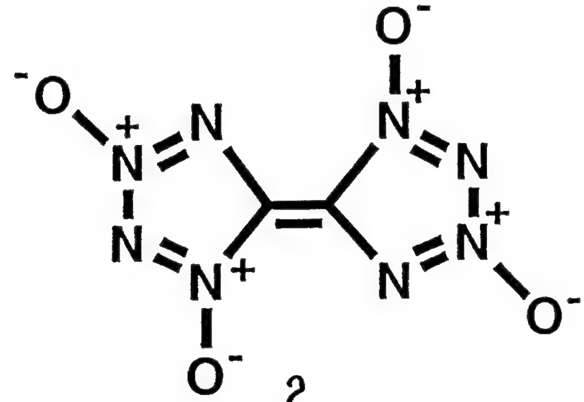

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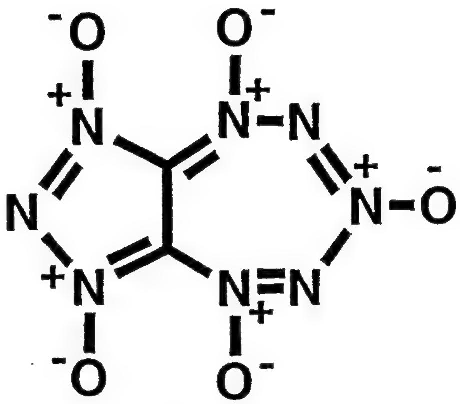
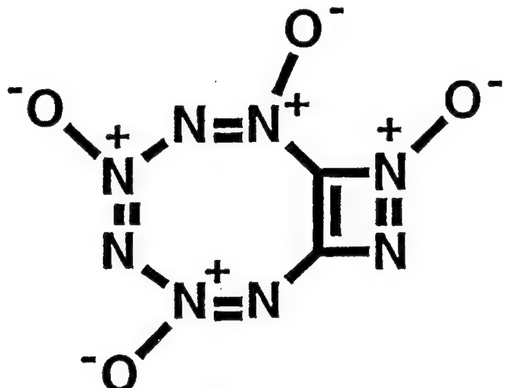


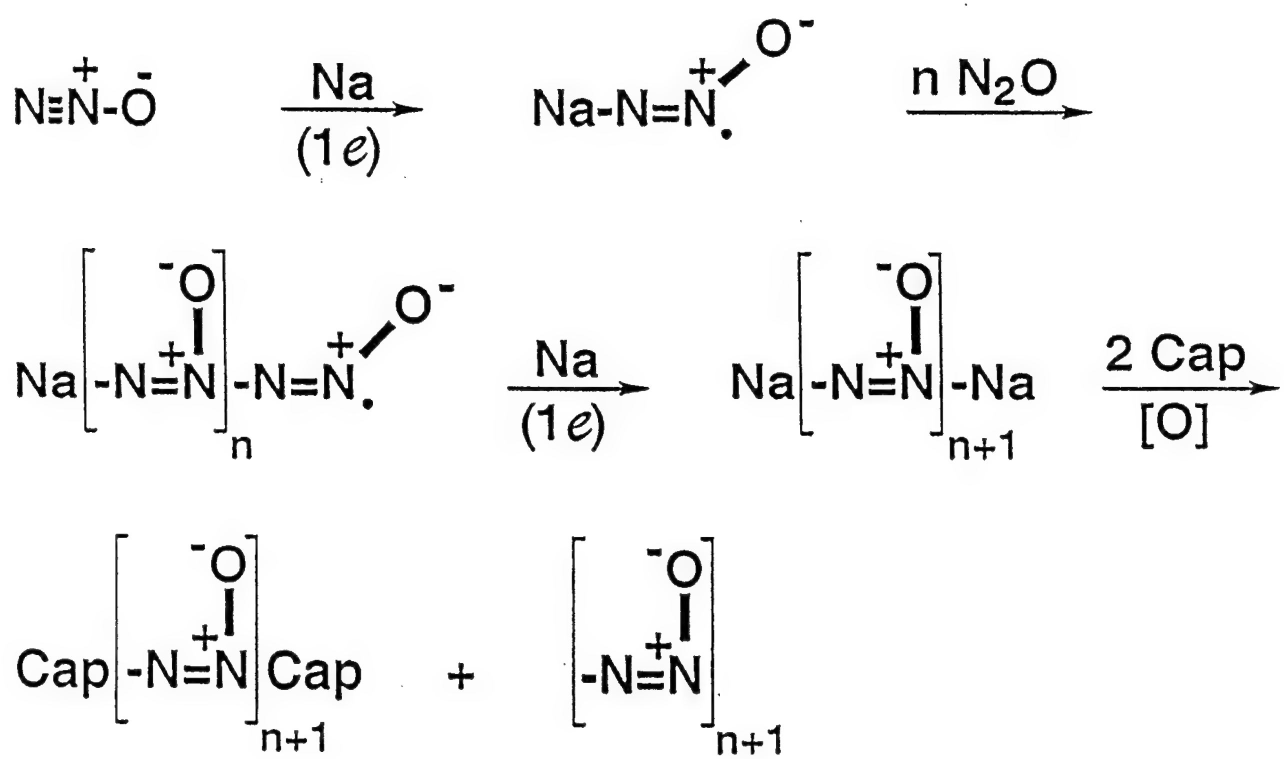
3



4

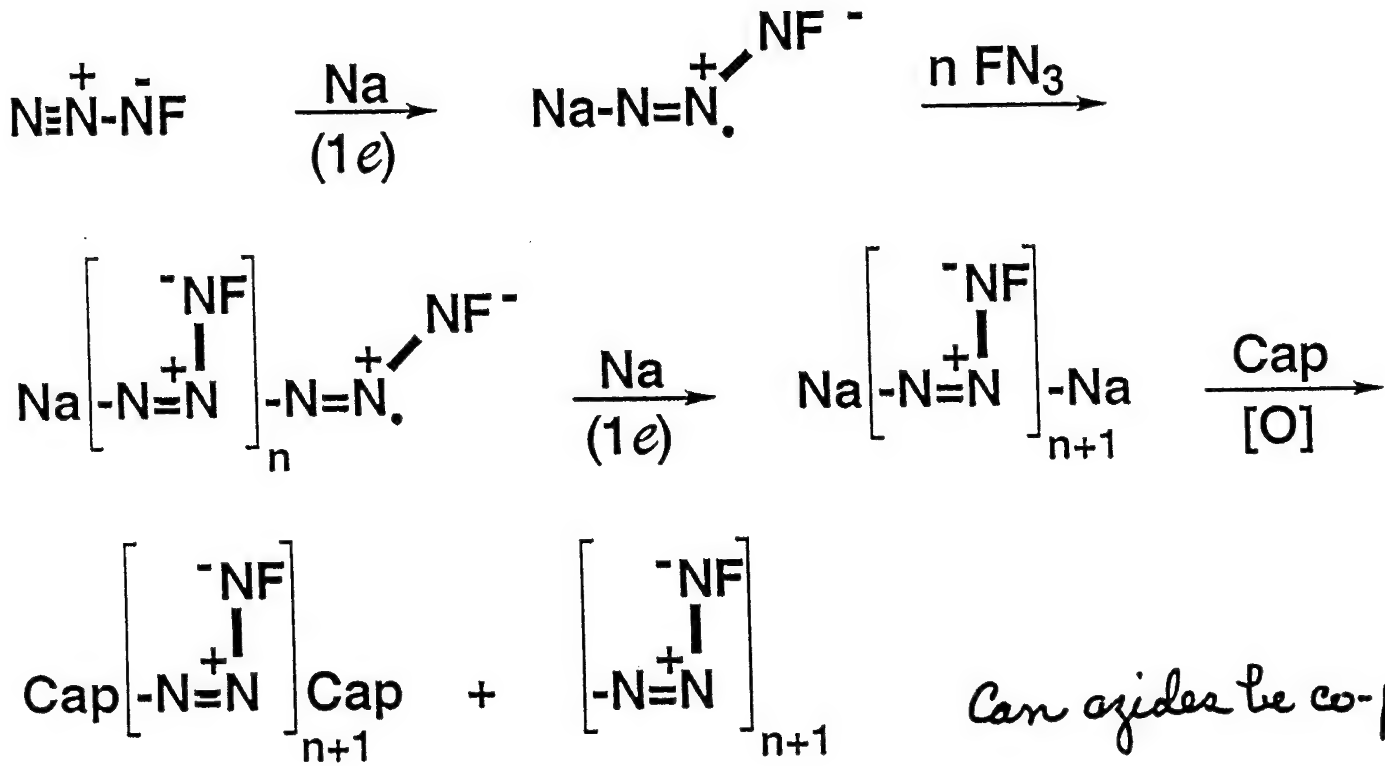
Compounds 1 and 2 are E + Z-isomers. Compounds 3 + 4 are also attractive. The theory and calculations of the molecules on slides 10 and 11 are to be developed. HS

Polymerization of Nitrous Oxide



Can N_2O and/or azides be polymerized or copolymerized?
Can N_2O undergo cyclooligomerization or cyclopolymerization?
N_2O adds to acetylenes to give α-diazoxides. Can N_2O and acetylenes be copolymerized?

Polymerization of Azides

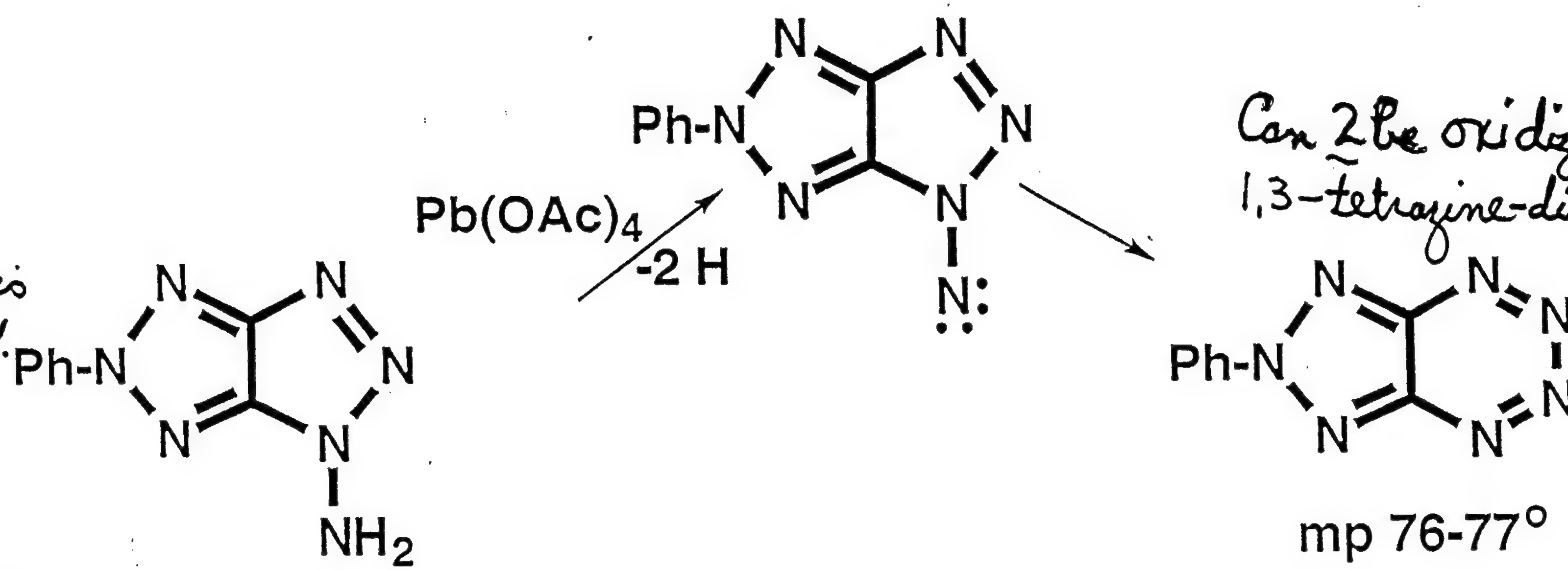


Can azides be co-polymerized?

$Z\text{-}N_3 = R_3Si\text{-}N_3,\ O_2N\text{-}N_3,\ NC\text{-}N_3,\ F\text{-}N_3$

This will be of great significance if accomplishable. Such programs should be initiated. Active metals add to N_2O!!

Stable [1,2,3]-Triazolo[1,2,3,4]tetrazines



1 2

Can 2 be oxidized to a 1,3-tetrazine-di-N-oxide?

[illegible] This molecule is readily prepared. Analogs should be studied. Substitute other groups for the phenyl substituent.

Triazolotetrazine 2 is preparable and fairly stable; It is the only known stable 1,2,3,4-tetrazine and its chemistry should be determined. Tetrazine 2 can not ring-open to a bis-diazo compound. The oxidation and derivatization of 2 should be studied. The phenyl group in 2 should be replaced by a removable group!!

Ohsawa, *Chem. Comm.*, 1988

Oxidation of Hydrazones with $Pb(OAc)_4$

$$R_2C{=}N{-}NH_2 \xrightarrow[\text{- }Pb(OAc)_2,\ \text{- 2 HOAc}]{Pb(OAc)_4,\ 10\text{-}25\ ^{\circ}C} R_2C{=}N{=}N$$

Stabilizing groups are highly electronegative and conjugating: RO_2C-, $-\overset{O}{\overset{\|}{C}}-$, $N{\equiv}C$, Ar, etc.

$$R_2C{=}N{=}N + HOAc \xrightarrow{\text{fast}} \underset{\sim 100\%}{R_2CH{-}OAc} + N_2$$

the acetic acid produced destroys diazo compounds unless they are highly stabilized (acid resistant).

Monohydrazones are rapidly oxidized to monodiazo compounds by lead tetraacetate. Unless the diazo compounds are stabilized by conjugating groups, they are decomposed very rapidly by the acetic acid produced. This method is not usable for synthesis of typical diazo compounds. Of interest is development of methodology in which the diazo compounds are not destroyed by acetic acid and elevated temperatures.

Oxidation of Hydrazones with $Pb(OAc)_4$ in Tetramethylguanidine/Dimethylformamide

$$R_2C{=}N{-}NH_2 \xrightarrow[\text{TMG, DMF, } -80\,^{\circ}\mathrm{C}]{Pb(OAc)_4} R_2C{=}N{=}N$$

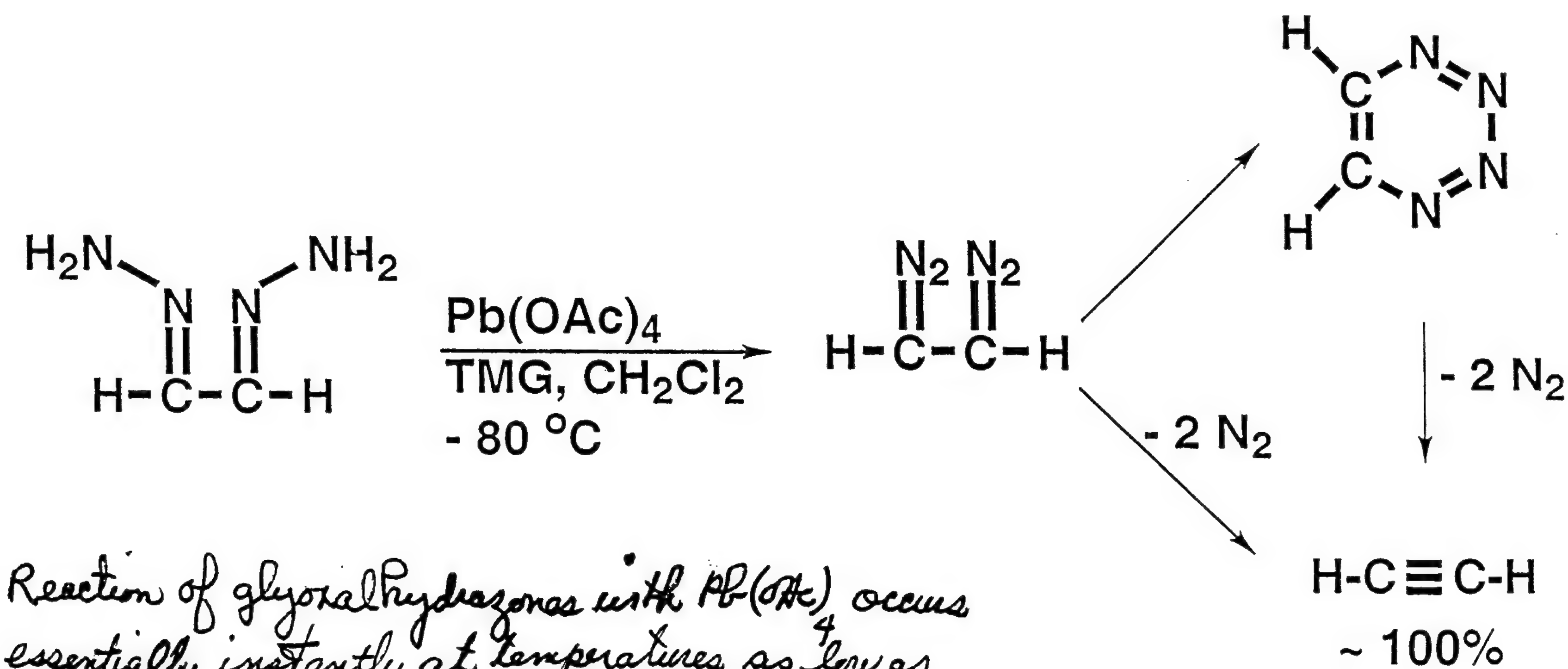
$TMG{=}(CH_3)_2N{-}C({=}NH){-}N(CH_3)_2$; $DMF{=}(CH_3)_2N{-}C({=}O){-}H$

Excellent General Method; J. Org. Chem., 1995

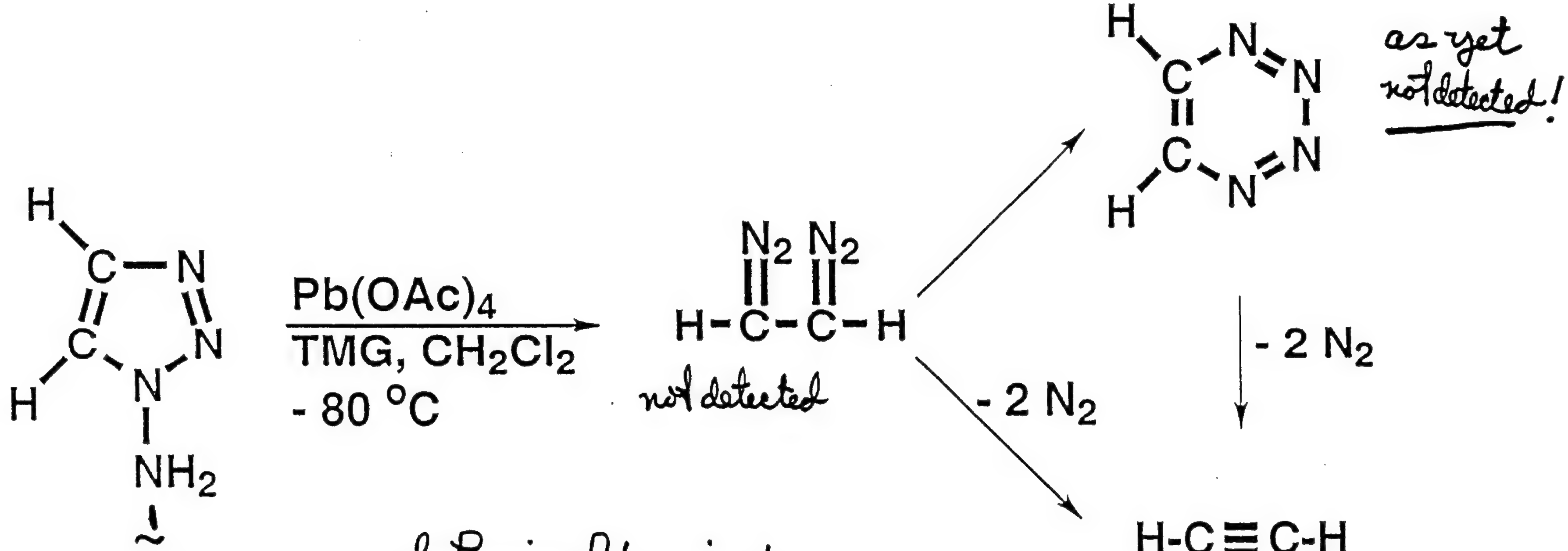
This method is the best known method for preparing monodiazo compounds at low temperatures. This method was originated and developed at Ohio State and published in 1995 as indicated. Of present interest and as sponsored by DARPA/AIR FORCE is extension of the method to vicinal-dihydrazones for practical syntheses of usable 1,2,3,4-tetrazines.

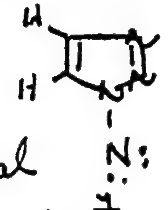
The TMG neutralizes the acetic acid and protects every diazo compound as it is prepared. Is the method usable for practical syntheses of vicinal bis-diazo compounds? The DMF serves as an excellent solvent for above reaction mixtures at low temperatures. The diazo compounds have been kept for days at -78°C.

Glyoxal Dihydrazones, $Pb(OAc)_4$, TMG, and CH_2Cl_2



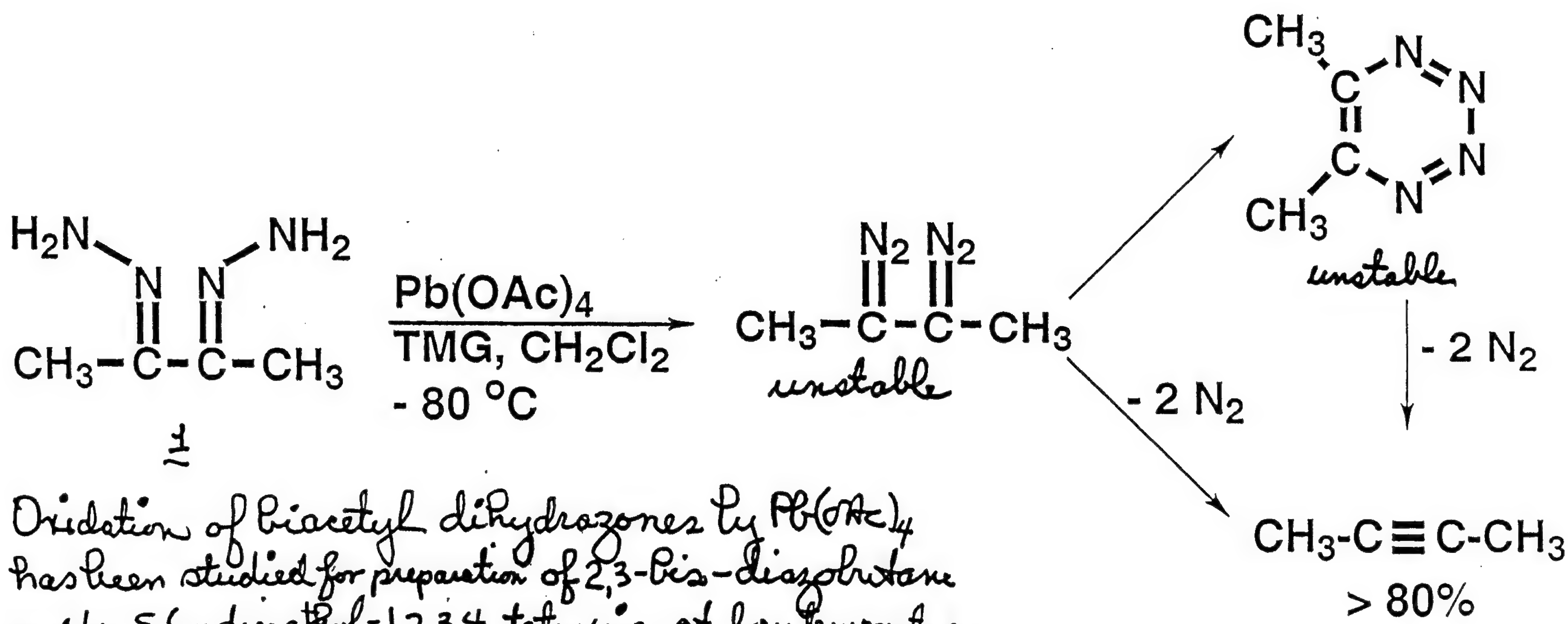
Reaction of glyoxal hydrazones with $Pb(OAc)_4$ occurs essentially instantly at temperatures as low as $-120°C$ to give acetylene essentially quantitatively. It is not known if 1,2,3,4-tetrazine is actually produced in these experiments. There are problems in these very low temperature oxidations in that the reagents are not very soluble. The oxidations should be tried in liquid CO_2 at low temperatures. Vanadium oxidants should be investigated.



Of interest are the oxidative behaviors of 1-amino-1,2,3-triazoles with Pb(OAc)$_4$ in TMG at low temperatures.
What is the behavior of 1-nitreno-1,2,3-triazole (1)
What is found  is that 1 decomposes with loss of 2 N_2 at < -80 °C.
The behavior above is identical with that for glyoxal dihydrazone in slide 19. 1,2,3,4-Tetrazine or 1,2-bis-diazoethane are unstable at < -80 °C and decompose rapidly to yield acetylene (~100%).

The system should be studied spectroscopically at low temperatures to detect intermediates and determine reaction mechanism.

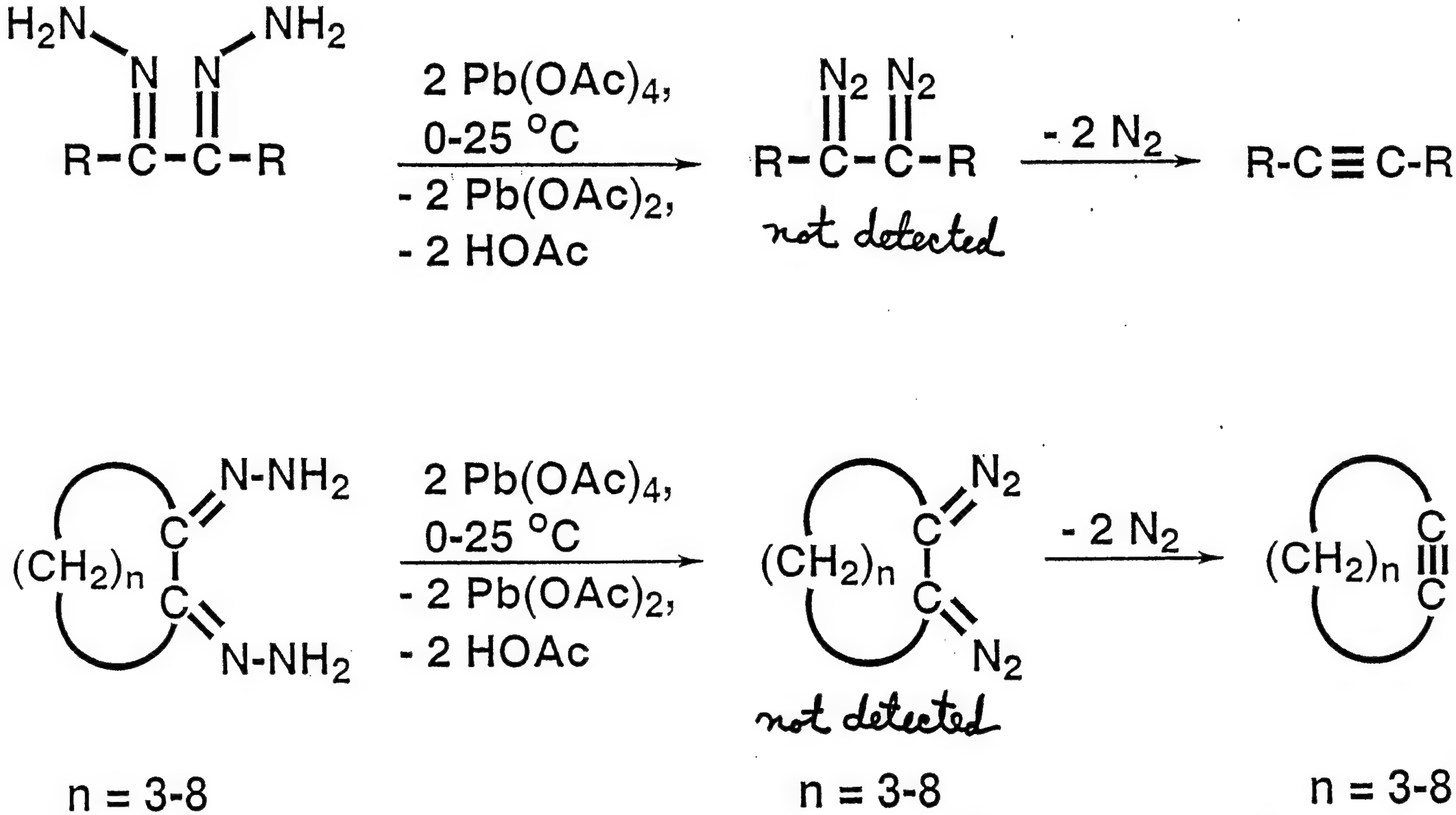
Biacetyl Dihydrazones, $Pb(OAc)_4$, TMG, and CH_2Cl_2



Oxidation of biacetyl dihydrazones by $Pb(OAc)_4$ has been studied for preparation of 2,3-bis-diazobutane and/or 5,6-dimethyl-1,2,3,4-tetrazine at low temperatures.

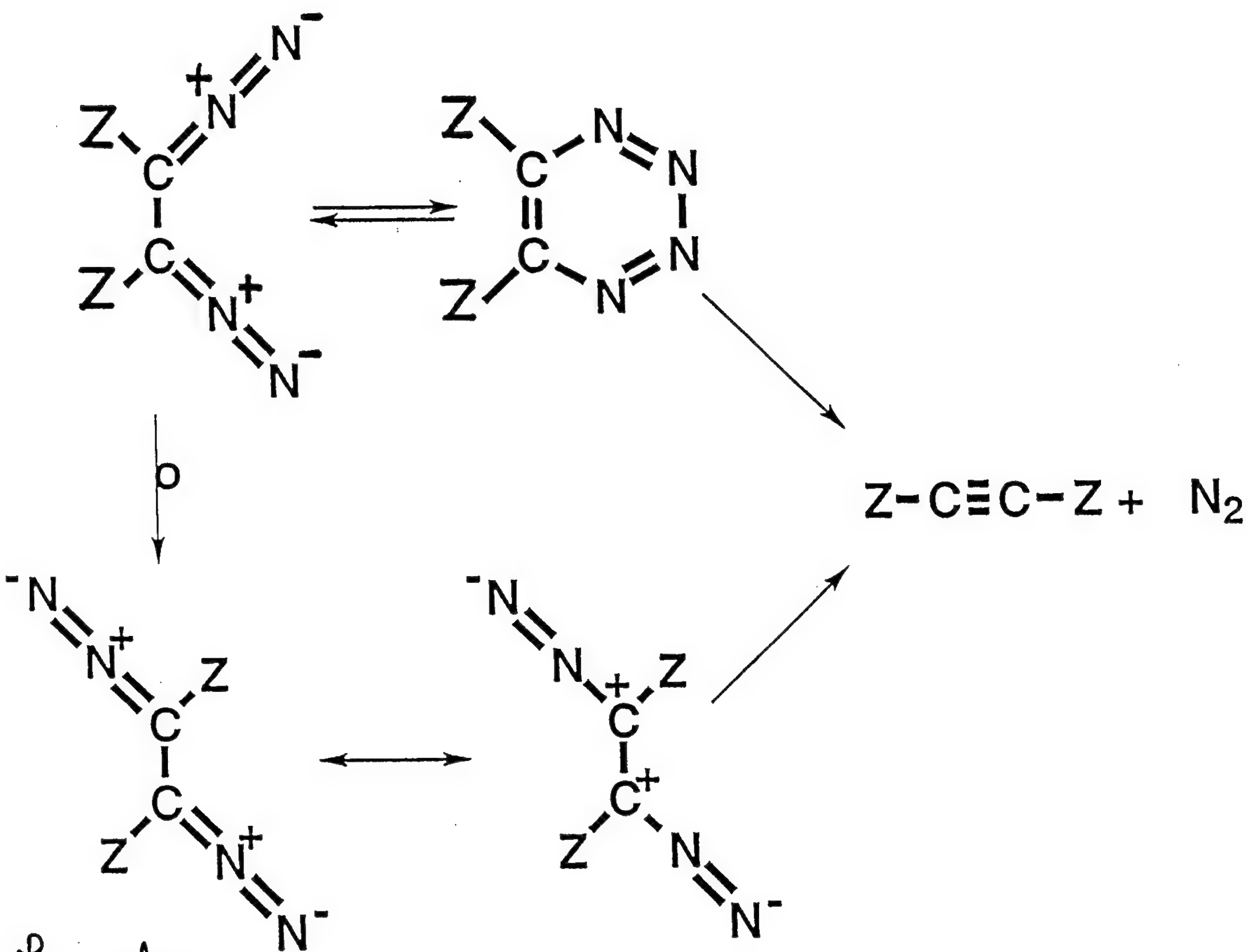
In all present experiments oxidation of 1 produces 2-butyne in > 80% yield essentially instantly (on adding the $Pb(OAc)_4$). The structures of the actual intermediates in the above experiments are as yet unknown!

Oxidation of *Vic*-Dihydrazones with $Pb(OAc)_4$



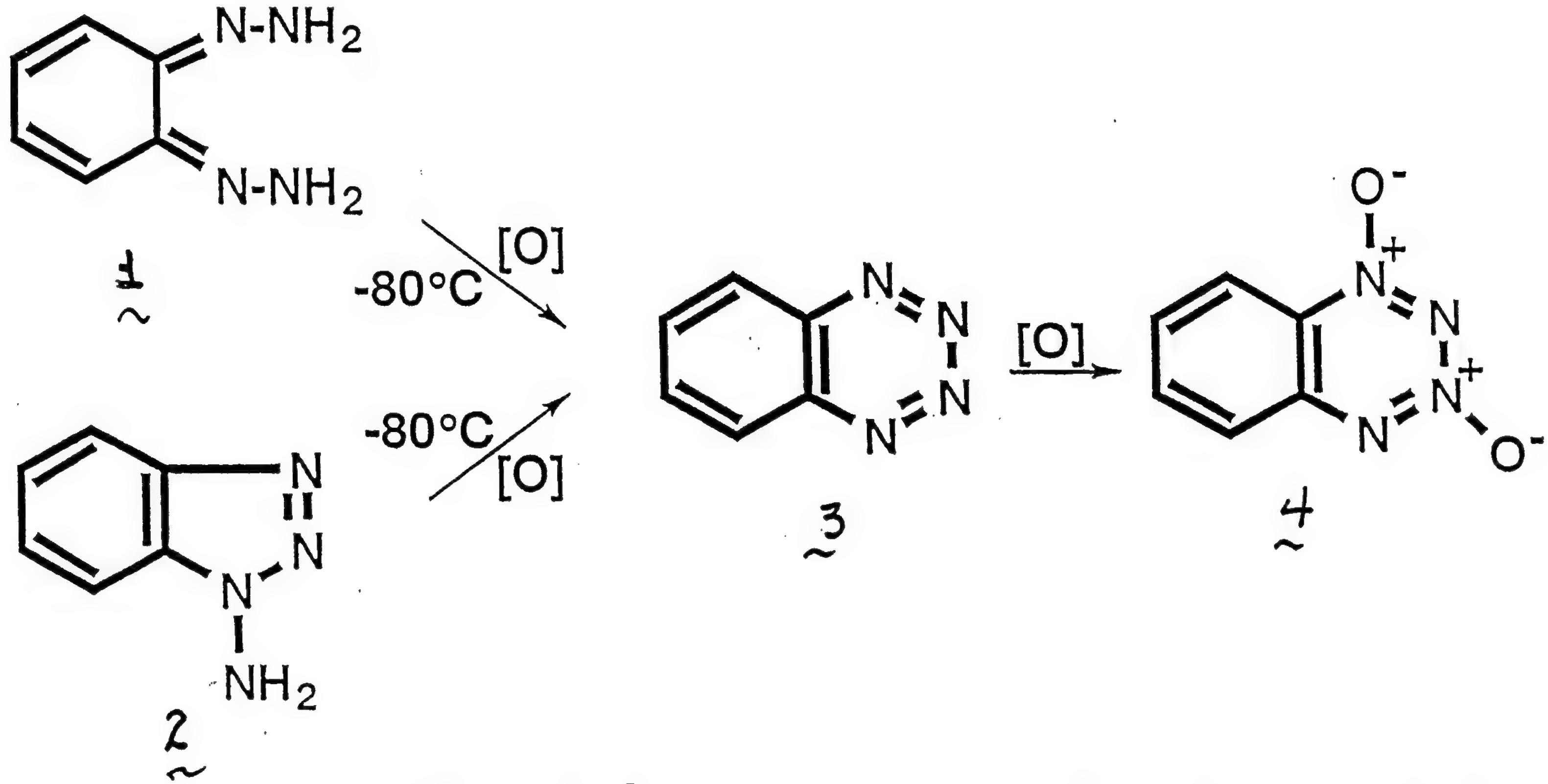
This overhead summarizes the results of oxidizing open-chain and cyclic vicinal dihydrazones with $Pb(OAc)_4$, TMG, and CH_2Cl_2. Acetylenes, even cyclopentyne, are produced in excellent yields. Of further interest is oxidation of 1,2-cyclobutanedihydrazone with $Pb(OAc)_4$. Can cyclobutyne be prepared? The strain in cyclobutyne will be enormous!

Vic-Bis-diazo Compounds or 1,2,3,4-Tetrazines



Why are bis-diazo compounds so unstable whereas mono-diazo compounds are not. Is stereochemistry very important? Are the 2 positive charges on adjacent carbon making the bis-diazo compounds so unstable? These results are very surprising.

Synthesis of Tetrazine 1,3-di-N-oxides

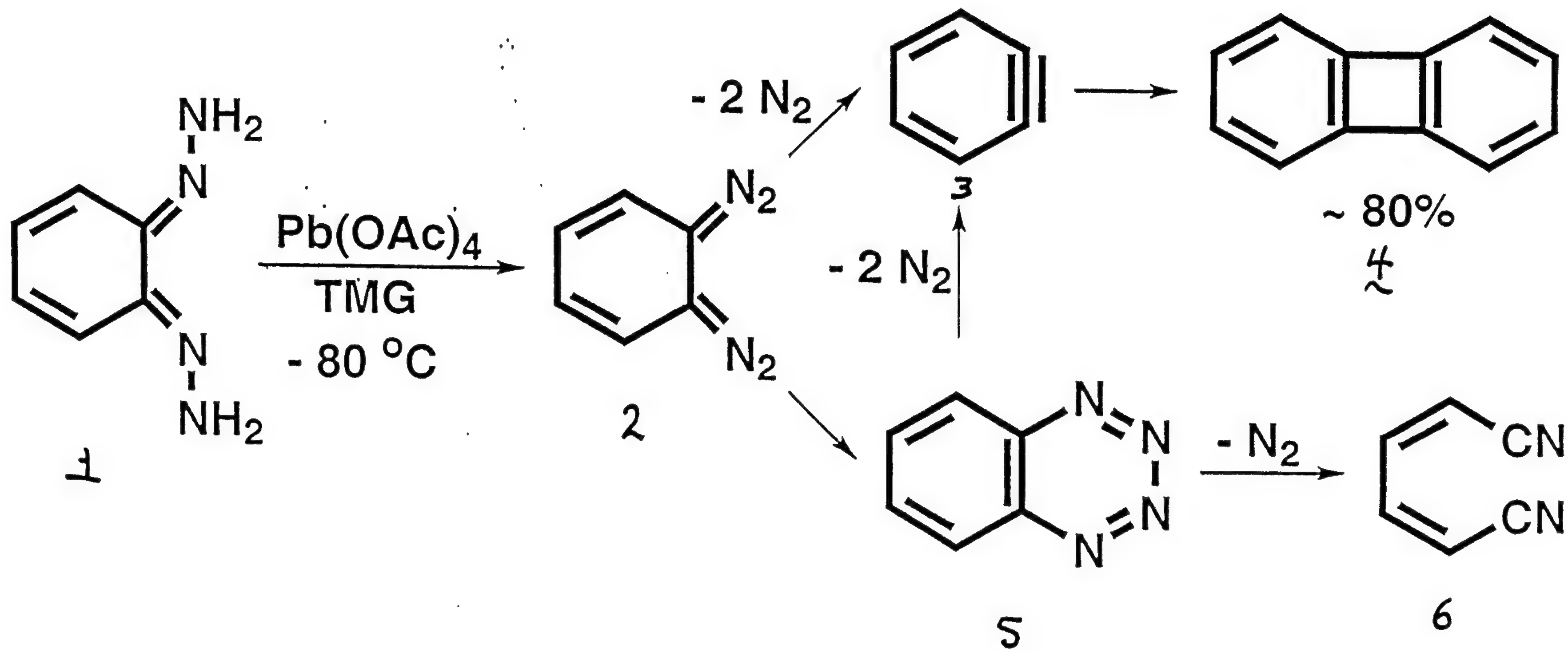


Study was initiated of possible oxidative-conversion of 1 and 2 to 3 as a possible practical source of 4. The oxidizing agent 6 is much more powerful

[O] = $Pb(OAc)_4$/TMG; $Pb(O_2CCF_3)_4$/TMG
5 6

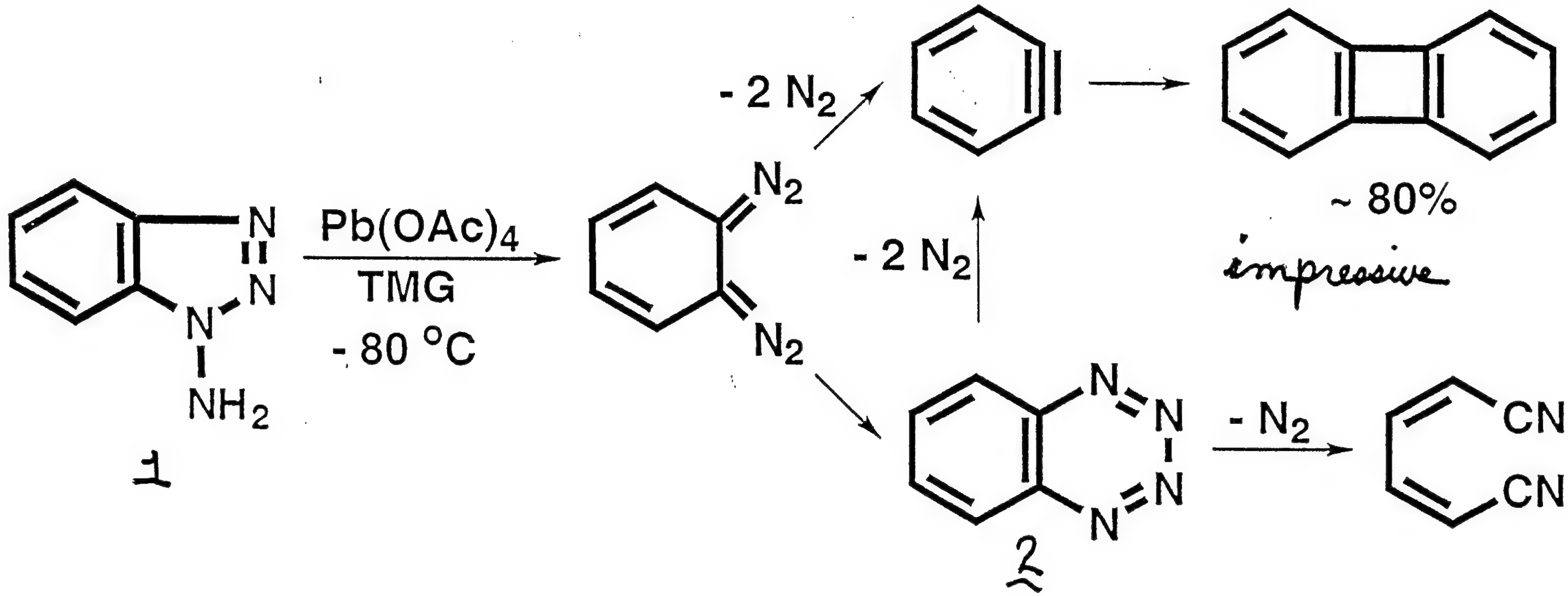
and can be used at lower temperatures than 5.

Oxidation of *o*-Quinone Dihydrazones with $Pb(OAc)_4$



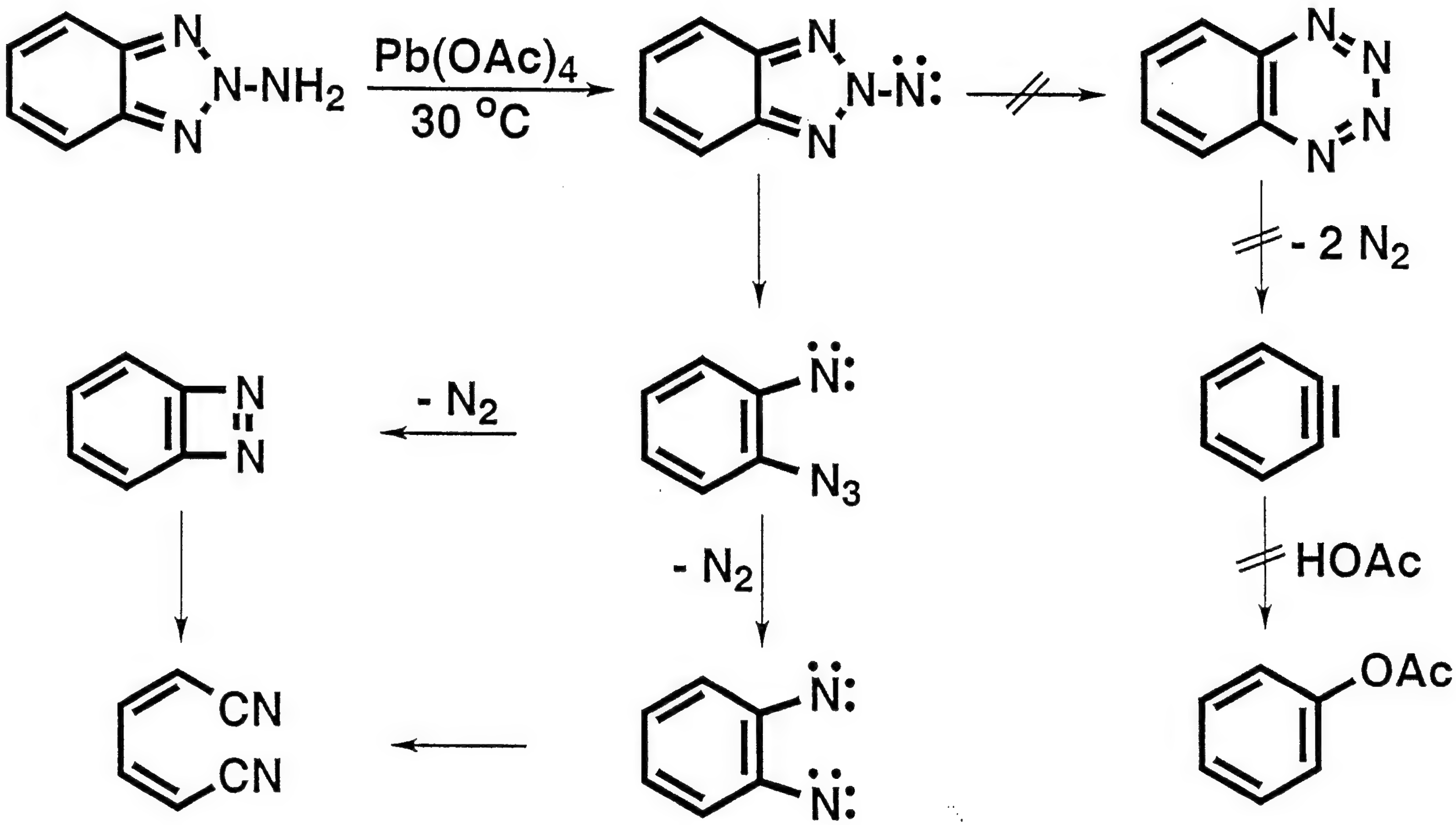
Investigation: Lower Temperatures; Solvents; IR; Oxidants; Traps

Oxidation of 1 by $Pb(OAc)$/TMG at temperatures as low as −100°C yields biphenylene (~80%) and 1,4-dicyano-1,3-butadiene (~20%). Benzotetrazine could not be detected. Can the oxidation be effected at lower temperatures??



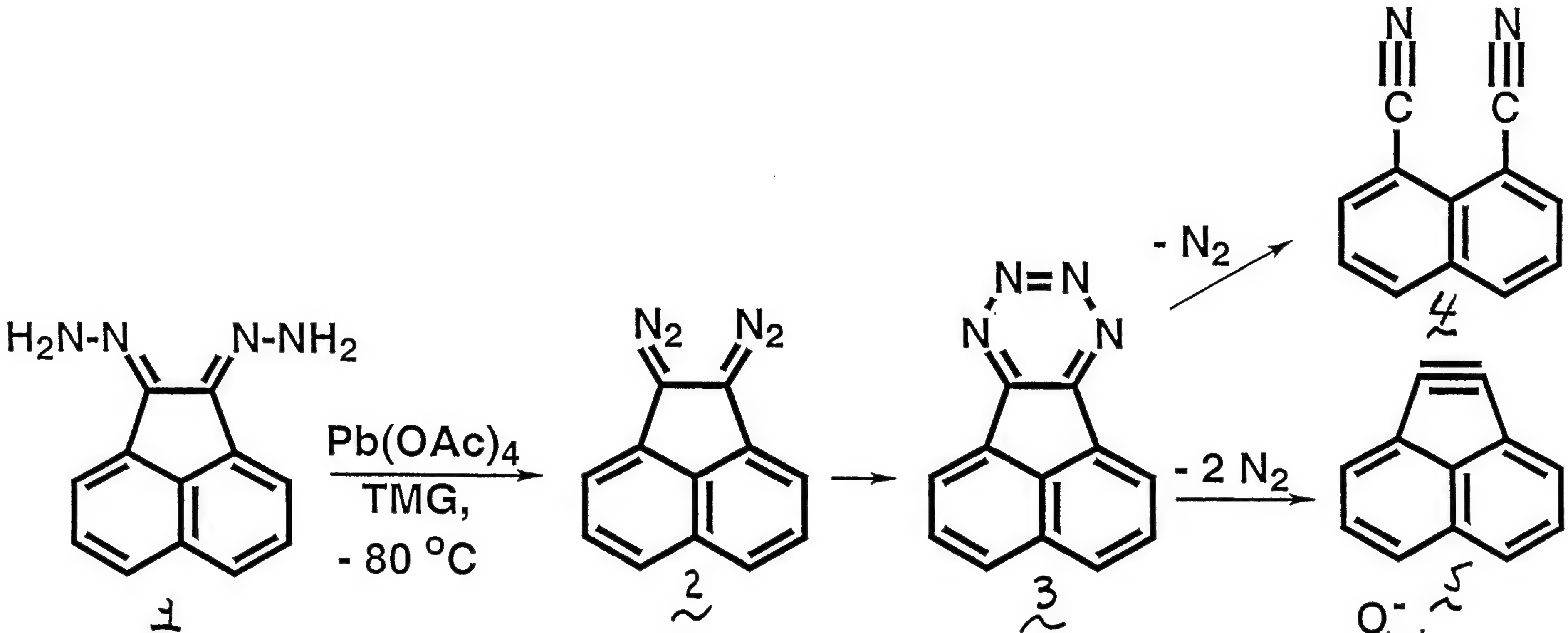
Of interest is the oxidative behavior of 1-aminobenzotriazole. Will the products of reaction of 1 be the same as in the previous overhead? The results are essentially identical; tetrazine 2 has as yet not been detected. Of note is that 1,4-dicyano-1,3-butadiene is formed!

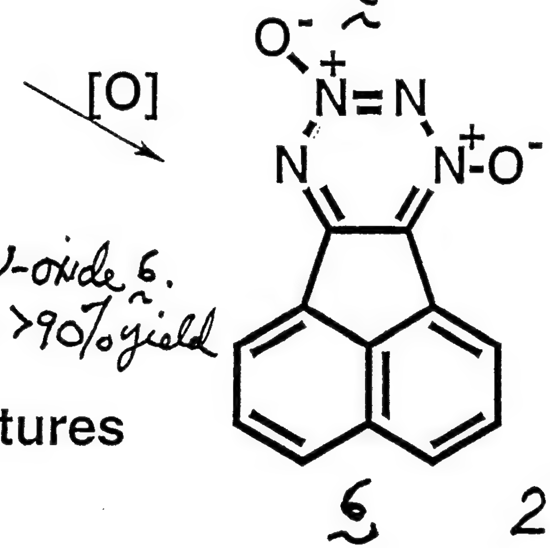
Oxidation of 2-Aminobenzotriazole



Of interest is the oxidative behavior of 2-aminobenzotriazole.
It has been presently found that oxidation of 2-aminobenzotriazole gives much more dicyano-1,3-butadiene than does 1-aminobenzotriazole.
The reaction intermediates are different.

Oxid'n of Acenaphthenequinone Dihydrazones with $Pb(OAc)_4$





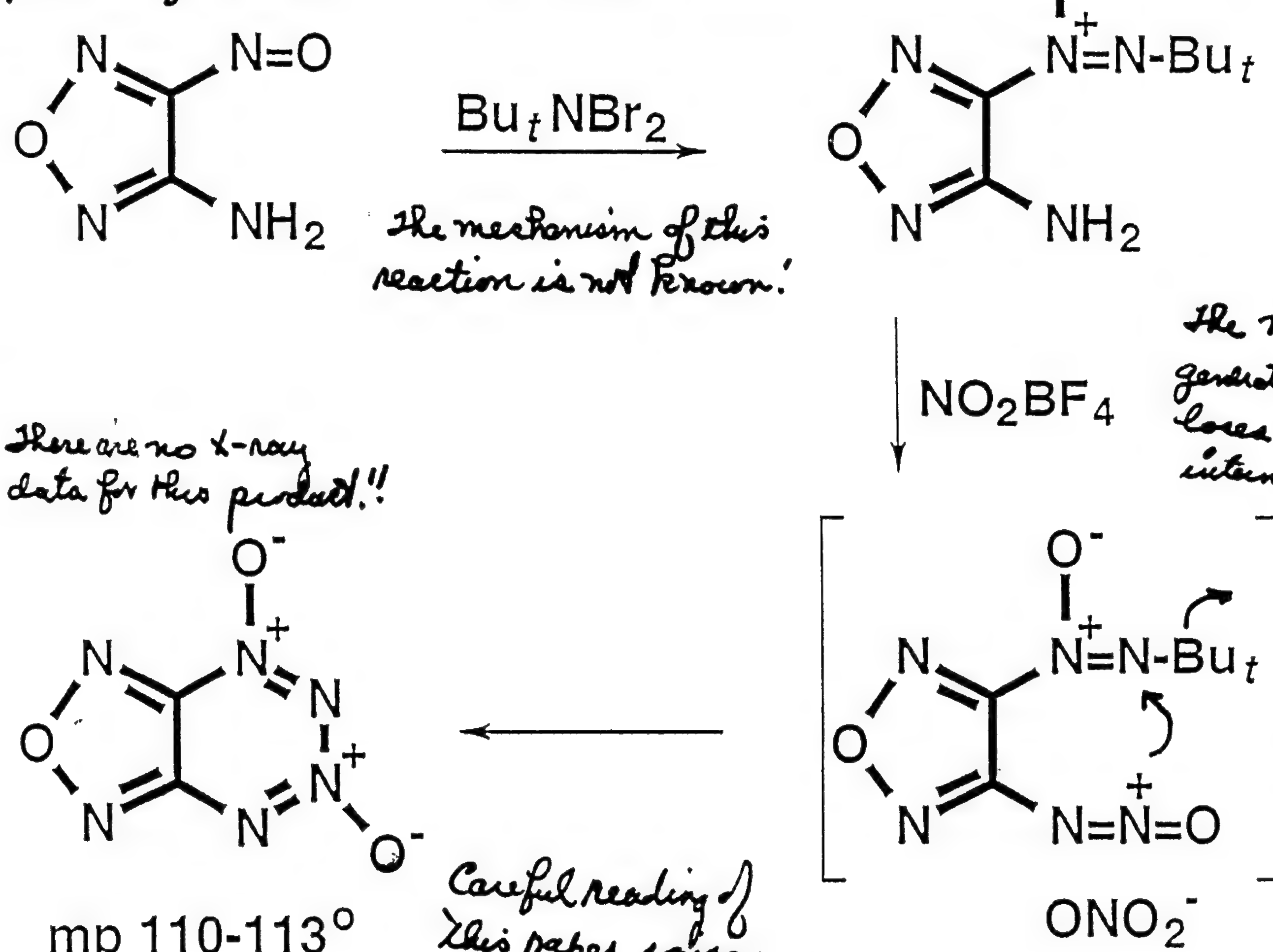
Of interest is oxidation of 1 to a stable bis-diazo compound 2, a stable 1,2,3,4-tetrazine 3, a stable acenaphthyne 5 and/or a product which might be converted to a simple tetrazine 1,3-di-N-oxide 6.
The facts: oxidation of 1 gives 4, a vicinal bis-dinitrile, in >90% yield

Investigation: Oxidants, Temperature, Solvents, Structures

Furazanotetrazine 4,6-Di-N-oxide (FTDO)

FTDO is now to be discussed because it is proposed to be usable for preparing DDTO or/and isoDDTO. FTDO was synthesized in the early 90s and was minimally described in a communication by Churakov at Zelinsky. The synthesis of FTDO is in a Ph.D. Thesis in Moscow! I want a copy of this thesis!

We will spend a lot of time on preparation of FTDO. FTDO is needed in large quantity!



The mechanism of this reaction is not known!

The nitramine is first generated which then loses OH^- to give the intermediate below.

There are no X-ray data for this product!!

note the methodology for ring closure! This is superb chemistry, if correct!

FTDO is minimally described in the paper cited. [Ch]urakovsky in his [E]ast Coast talk [s]ummarized this [sy]nthesis of FTDO!

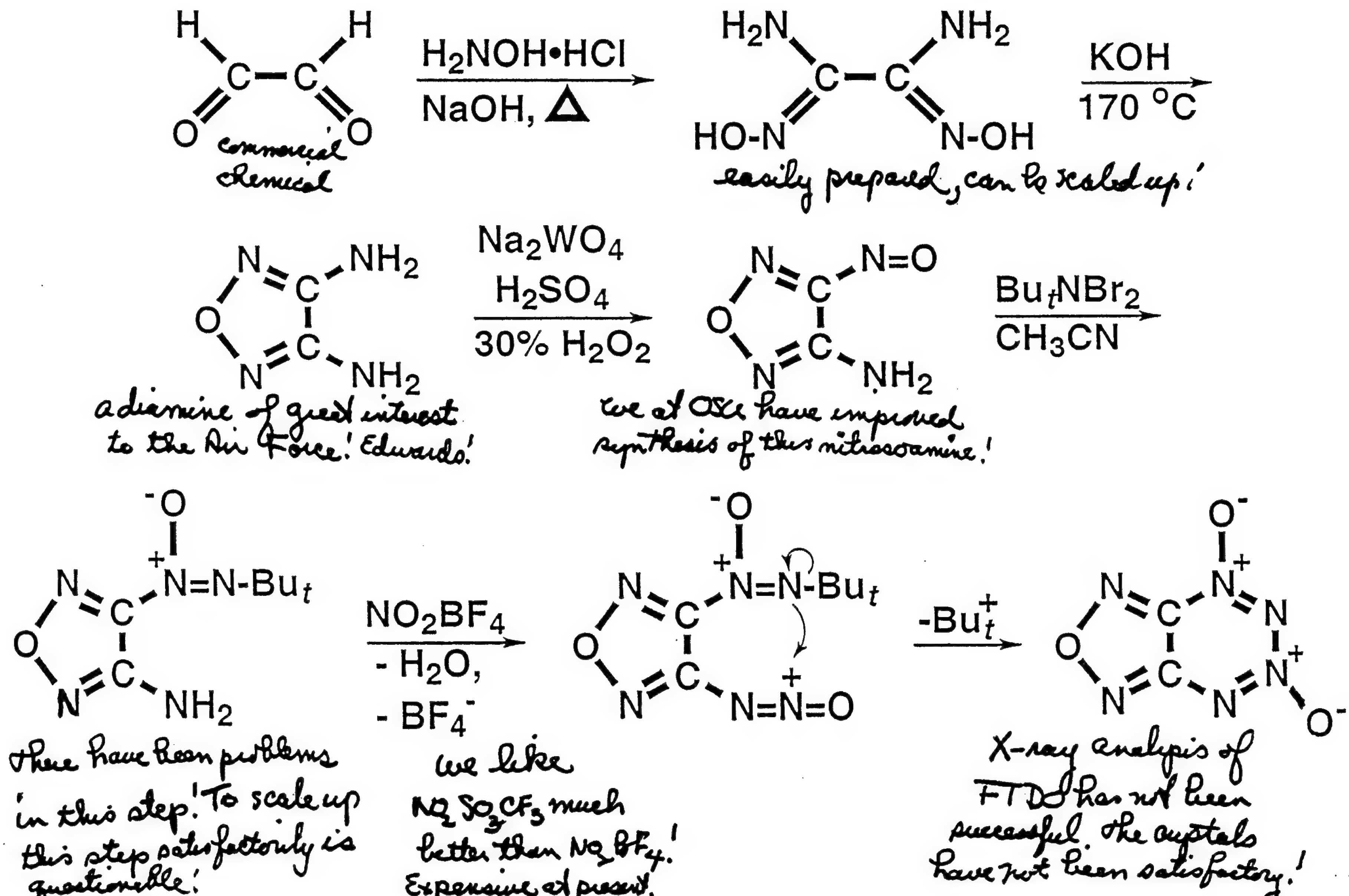
Careful reading of this paper raises problems as to how reliable the Russian synthesis is!!

Churakov et al, Tetrahedron, 1995

The method for preparing FTDO is based on that to be described much later for benzotetrazine 1,3-di-N-oxide.

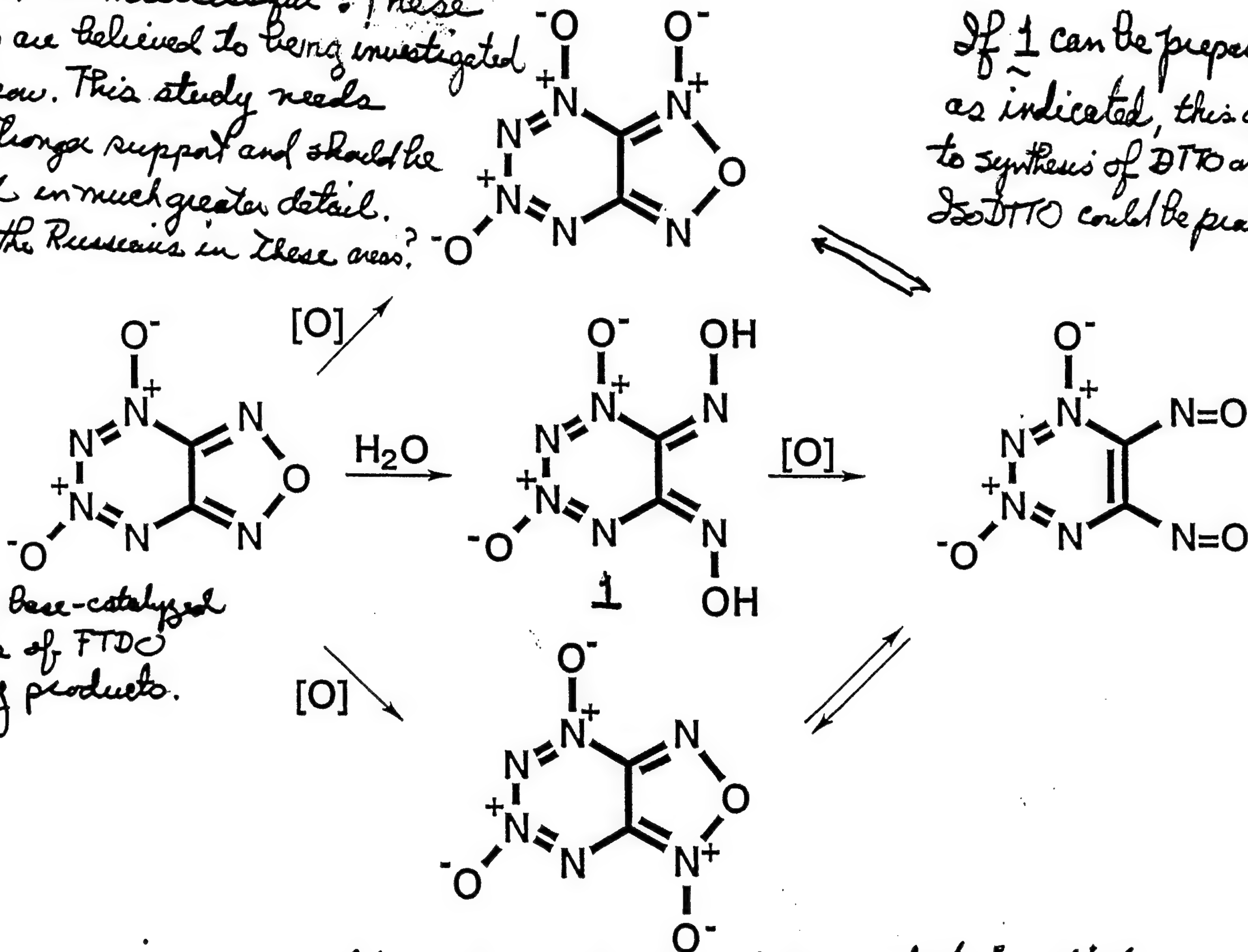
This is a summary of the Russian and now a OSU synthesis of FTDO. Preparation of FTDO has been difficult! The CIA or someBody should have scanned a Russian thesis describing the final step in the synthesis.

Furazanotetrazine 4,6-Di-N-oxide (FTDO)



The following transformations of FTDO have not been successful. These reactions are believed to being investigated in Moscow. This study needs much stronger support and should be discussed in much greater detail. Where are the Russians in these areas?

If $\underset{\sim}{1}$ can be prepared as indicated, this approach to synthesis of DTTO a/and IsoDTTO could be practical.

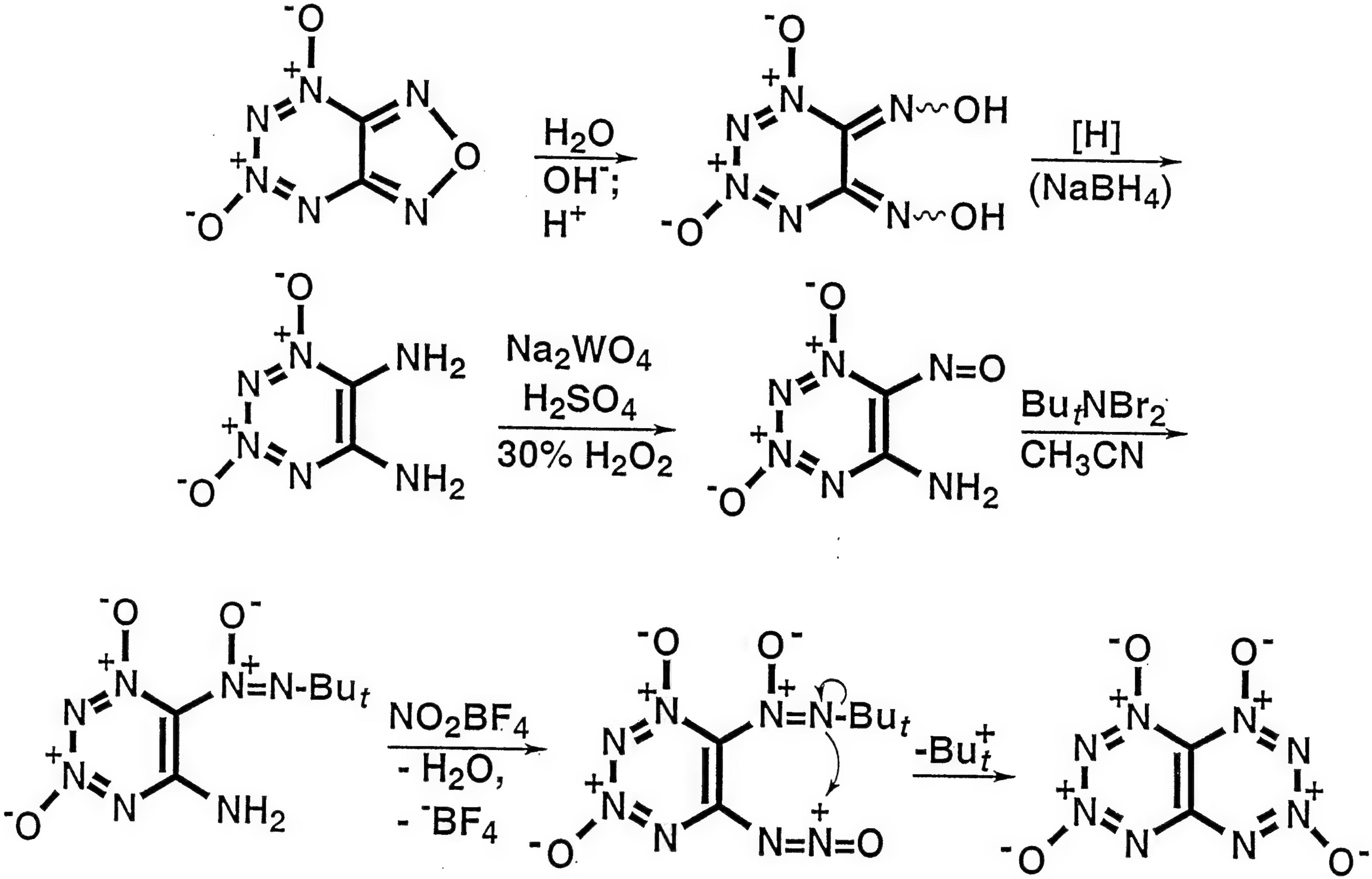


acid- and base-catalyzed hydrolyses of FTDO give many products.

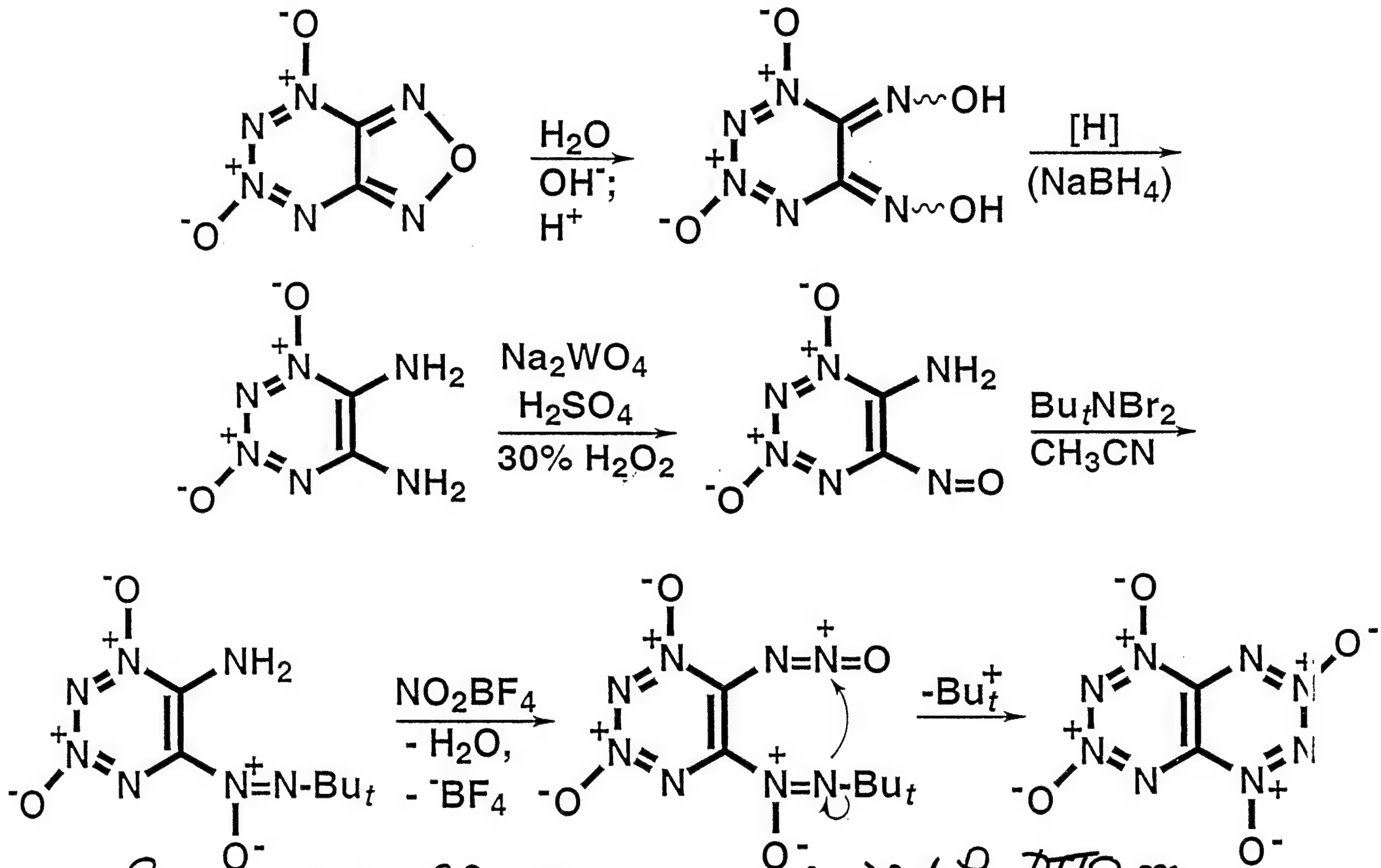
This is an important project! We have not had sufficient support to investigate the above project properly. "Zelinski" has had a 10-12 year head start on this project.

This overhead summarizes the present route proposed for DTTO at ?. Are the Russians studying this route? We believe so.

Proposed Synthesis of DTTO

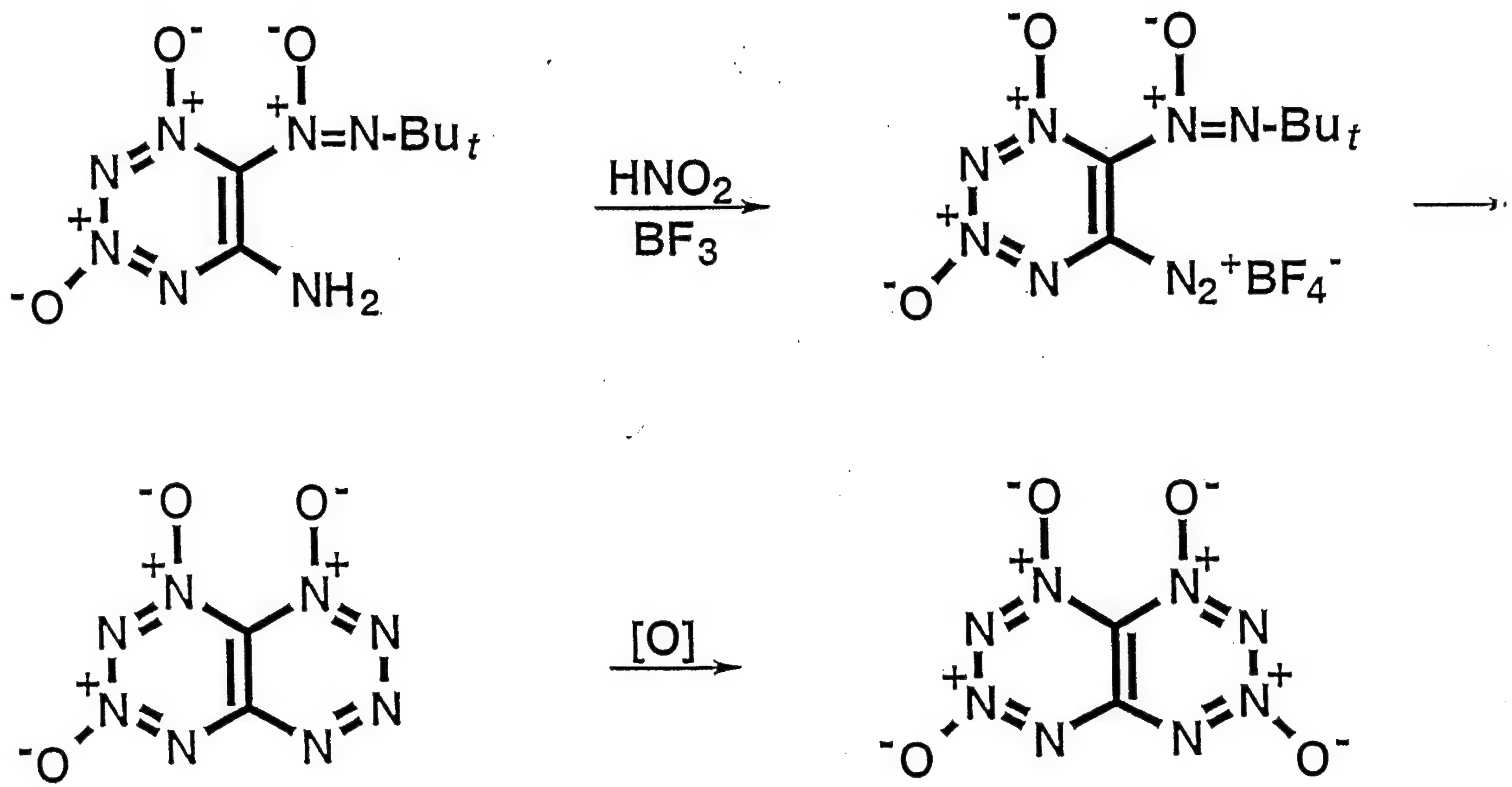


Proposed Synthesis of IsoDTTO



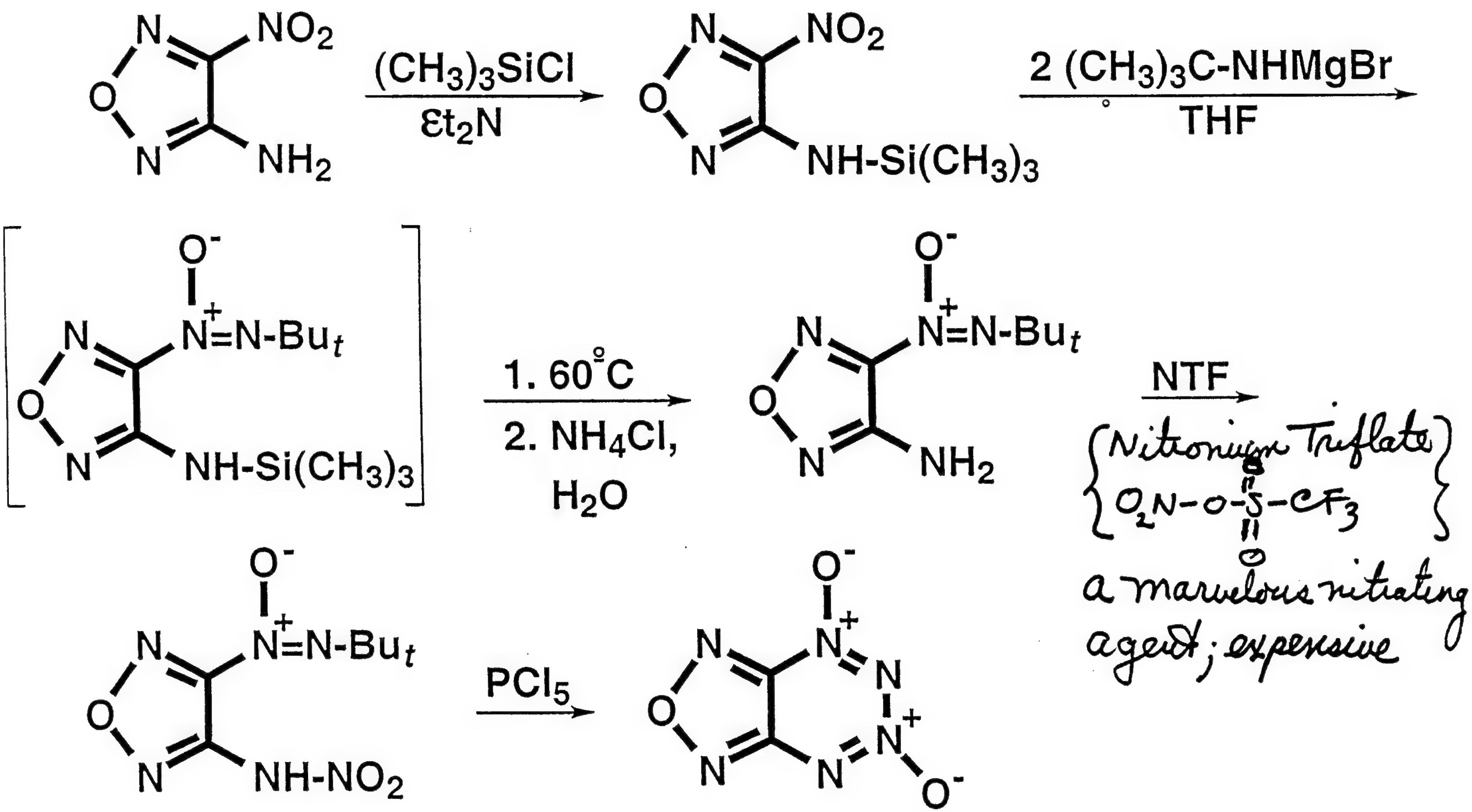
This synthesis of IsoDTTO parallels that for DTTO on the previous overhead. The key is successful ring-opening of FTDO!

Proposed Synthesis of DTTO



This is an alternate synthesis of DTTO. This ring-closure is different than that proposed previously. This sequence also proposes initial preparation of a 1,2,3,4-tetrazine-1-oxide which is stable.

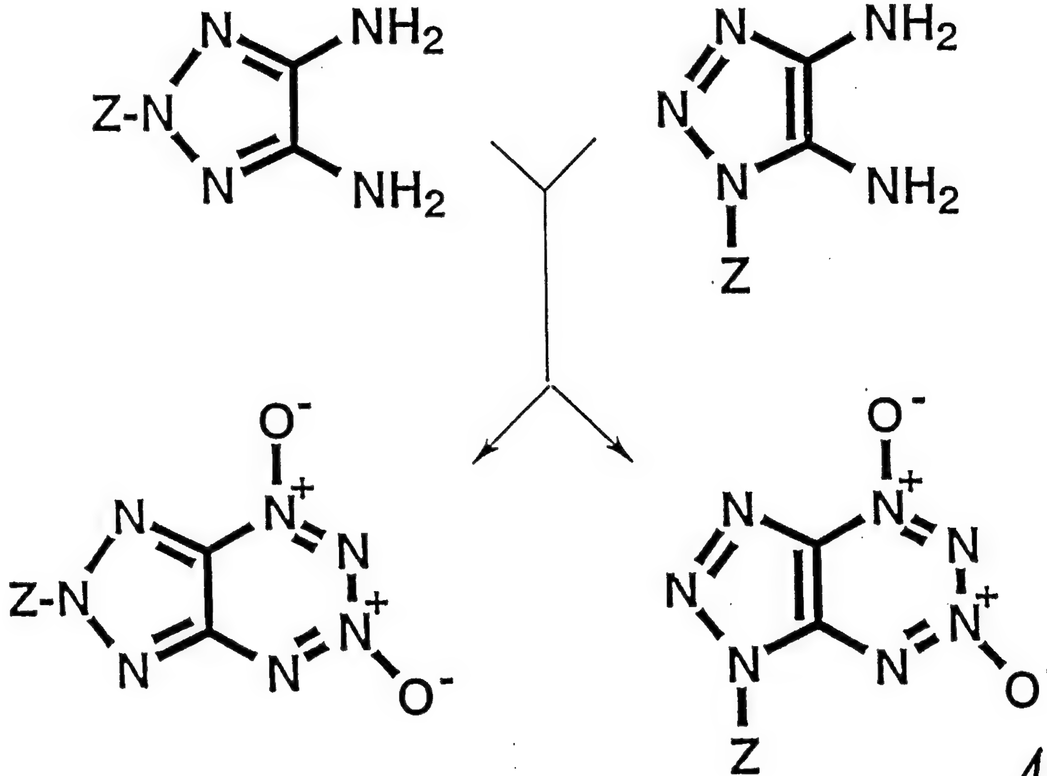
Furazanotetrazine 1,3-Di-N-Oxide



OHIO STATE

This is a major advance in synthesis of FTDO!

Synthesis of Triazolotetrazine 1,3-Dioxides

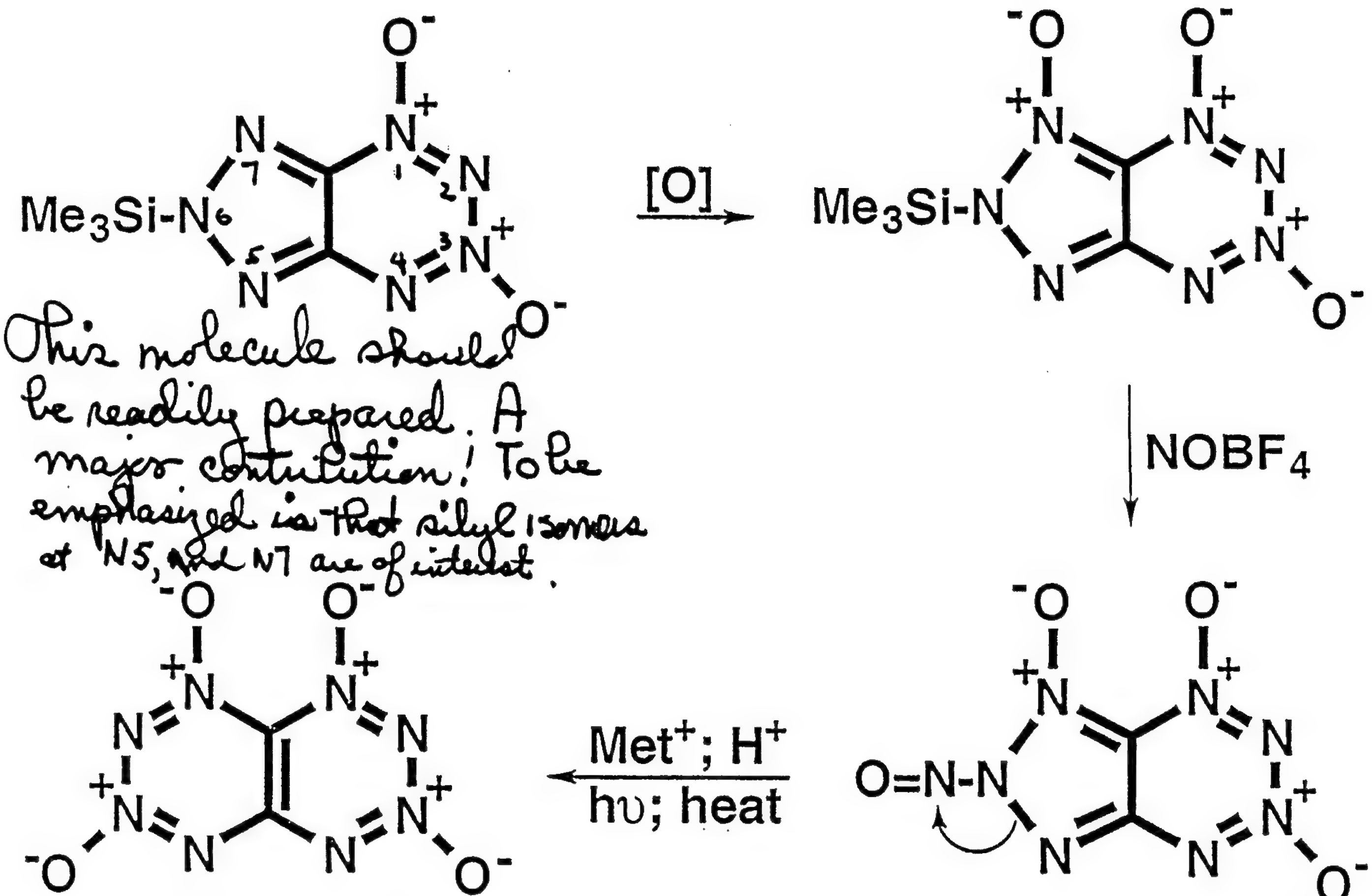


$Z = H, SiR_3, R\text{-}SO_2, R\text{-}C(=O), CN$

Are these sequences being investigated in Russia?

These synthesis routes are now to be studied.
This effort will have to be funded soon.
Very practical chemistry might come from these sequences.
These sequences have been initiated at ASU.

Possible Synthesis of DTTO

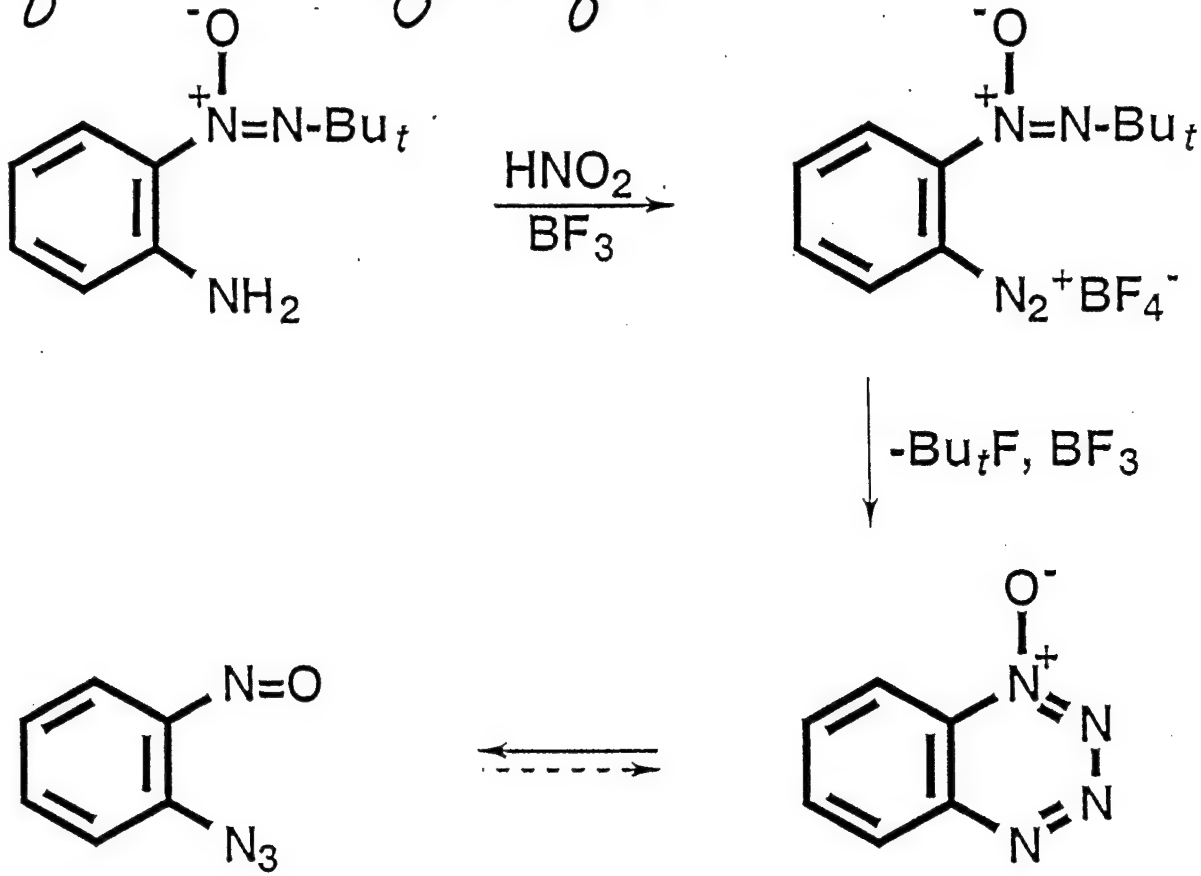


This molecule should be readily prepared. A major contribution! To be emphasized is that silyl isomers at N5, and N7 are of interest.

A possible practical synthesis of DTTO as yet not investigated. This is a major and important project. To be discussed further if possible

Synthesis of Benzotetrazine 1-N-Oxide

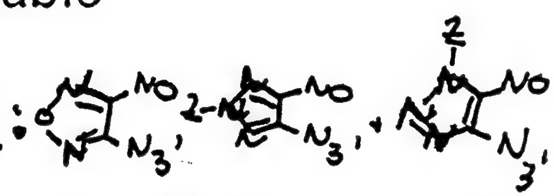
This overhead illustrates the first publication by Zelinsky for synthesis of a stable benzotetrazine oxide!



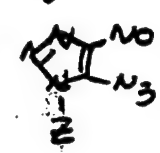
fairly stable

we know little about o-nitroso azides.

This is an important concept.
Various heterocyclic (5 and 6-membered ring) ortho nitroso azides should be evaluated:

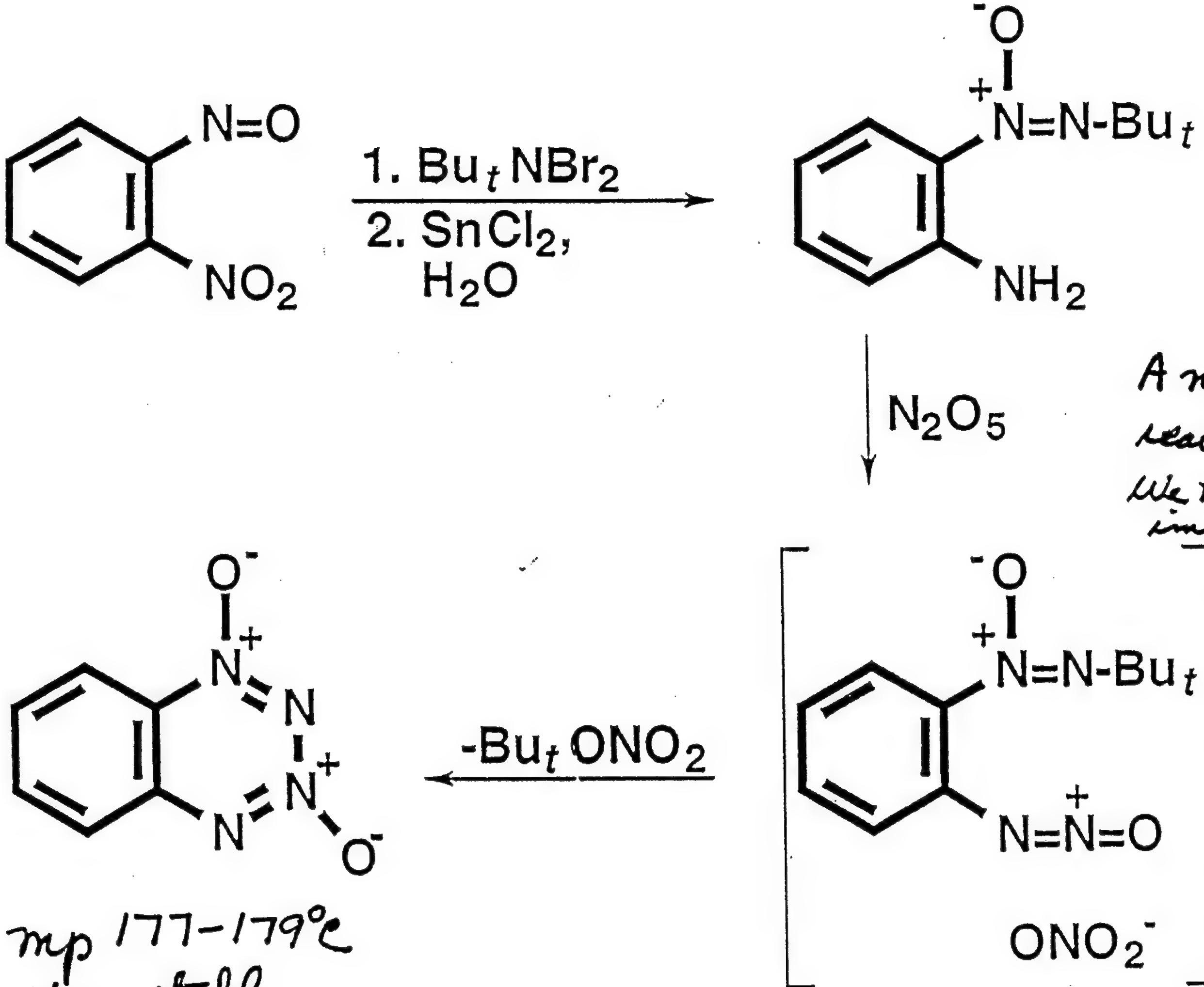


and



Do the molecules proposed exist in ring-open or ring-closed forms?

Synthesis of Benzotetrazine 1,3-Di-N-oxide



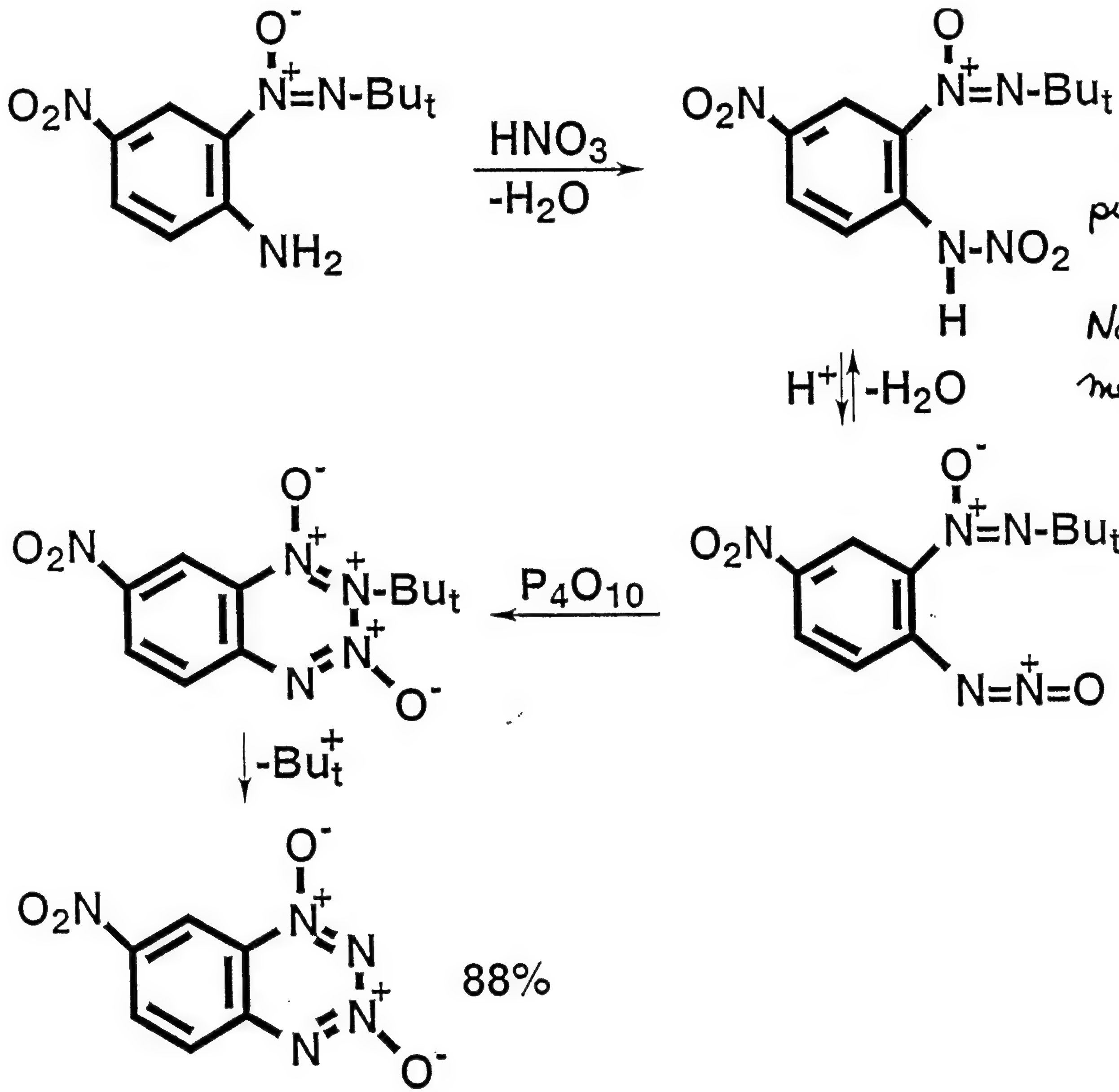
A nitramine is the reaction intermediate! We have repeated and improved this synthesis.

An enormous contribution! This has led to the tremendous effect in Moscow on high-nitrogen chemistry.

mp 177–179°C
Very stable

Churakov, Mendel. Comm. 1991

This is a very important paper, that was ignored in the US.



(Use of P_4O_{10} on primary nitramines).

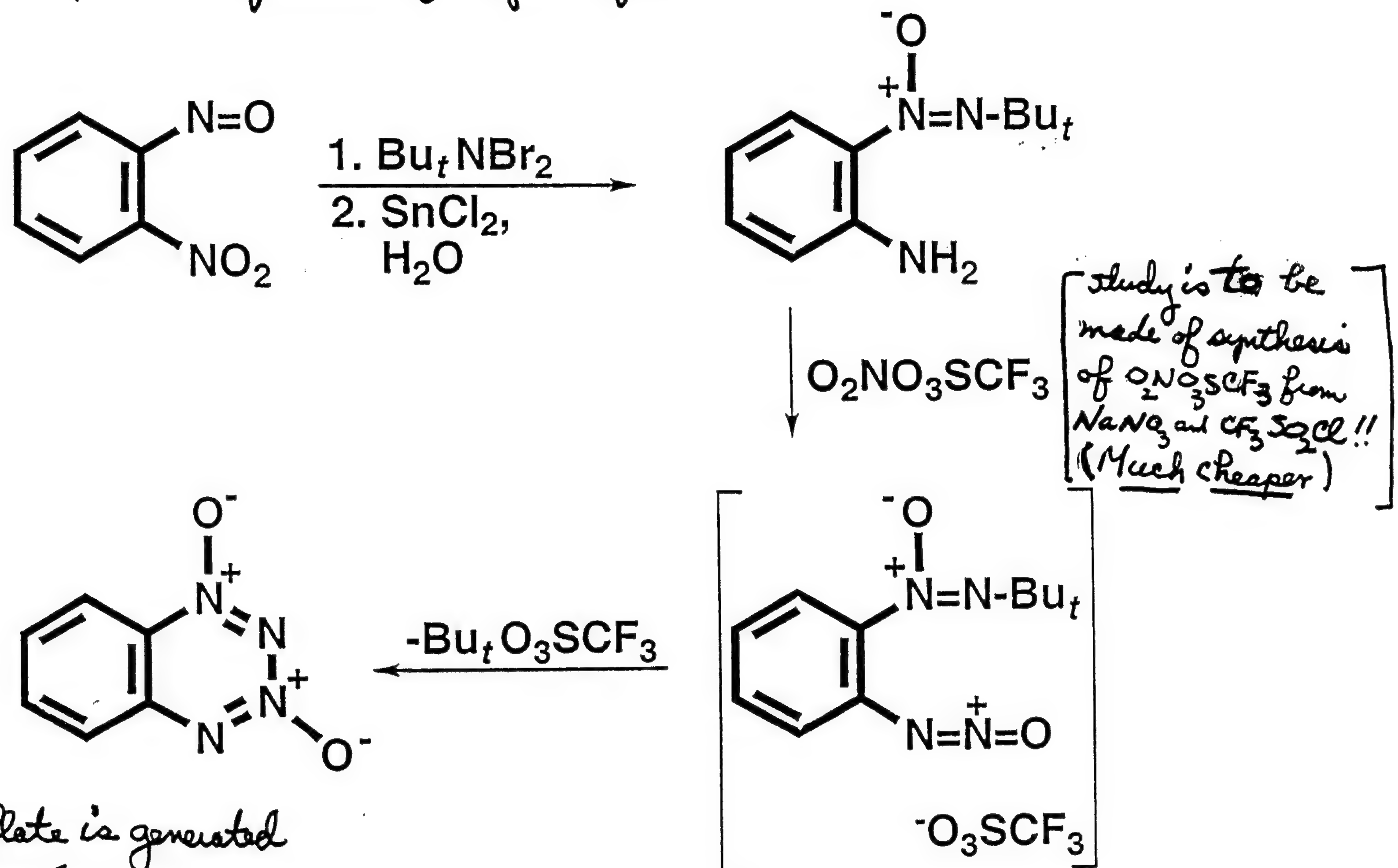
Note the improved methodology.

Frumkin et al, *Russ. Chem. Bull.* 2000, *49*, 482

This publication extends and improves the previous methodology for preparing benzotetrazine 1,3-di-N-oxides.

Synthesis of Benzotetrazine 1,3-Di-N-oxide

an improved synthesis of benzotetrazine 1,3-di-N-oxide



[study is to be made of synthesis of $O_2NO_3SCF_3$ from $NaNO_3$ and CF_3SO_2Cl!! (Much cheaper)]

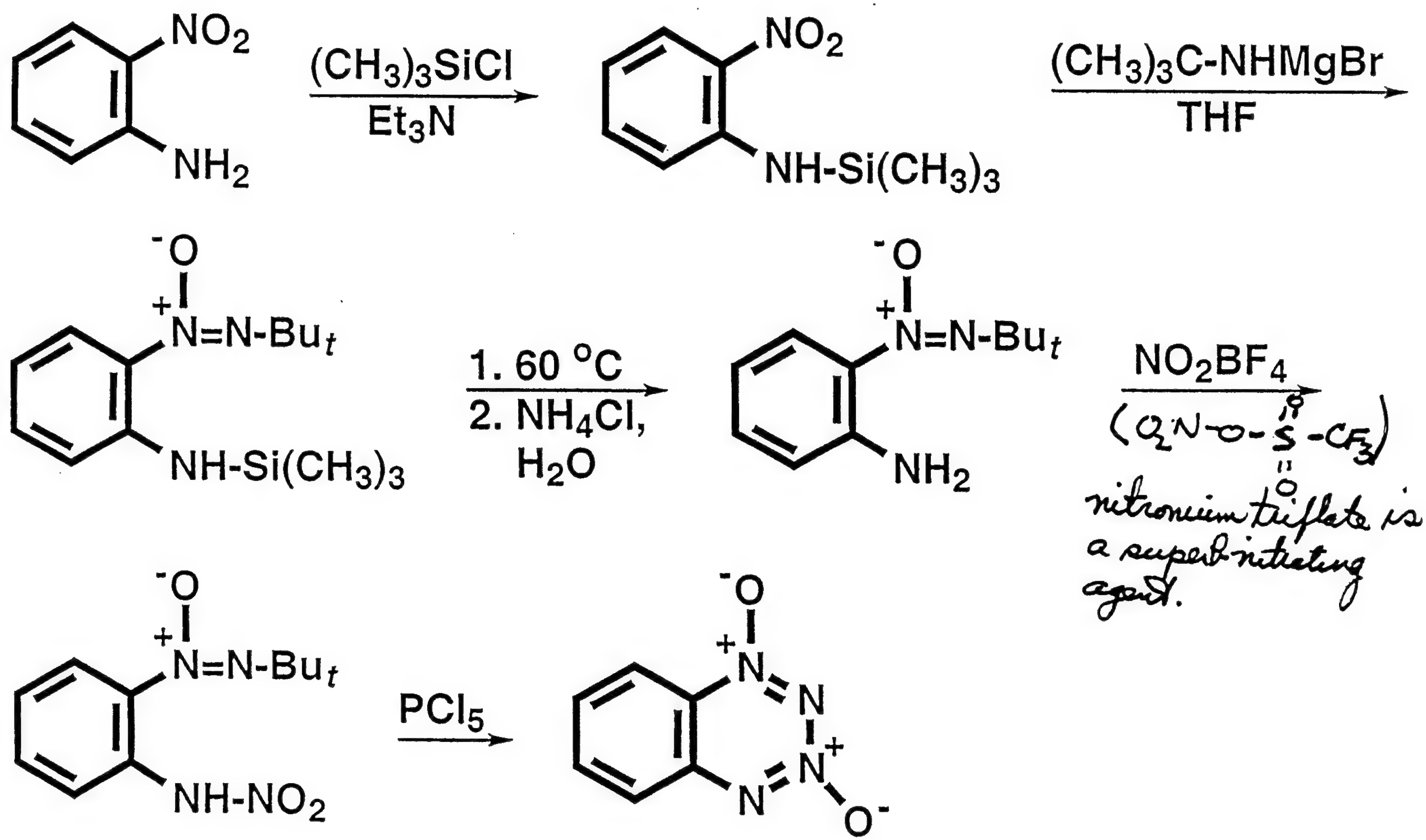
Nitronium triflate is generated from $(CH_3)_4N^+NO_3^-$ and $(CF_3-SO_2)_2O$; the Shackelford method.

OHIO STATE, 2003

The major contribution at OSU is use of nitronium triflate.

Benzotetrazine 1,3-Di-N-oxide

A new method for preparing benzotetrazine 1,3-di-N-oxide

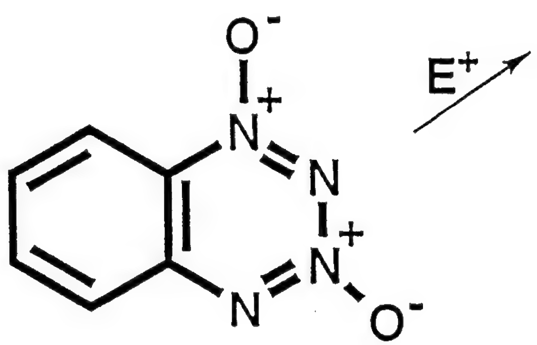


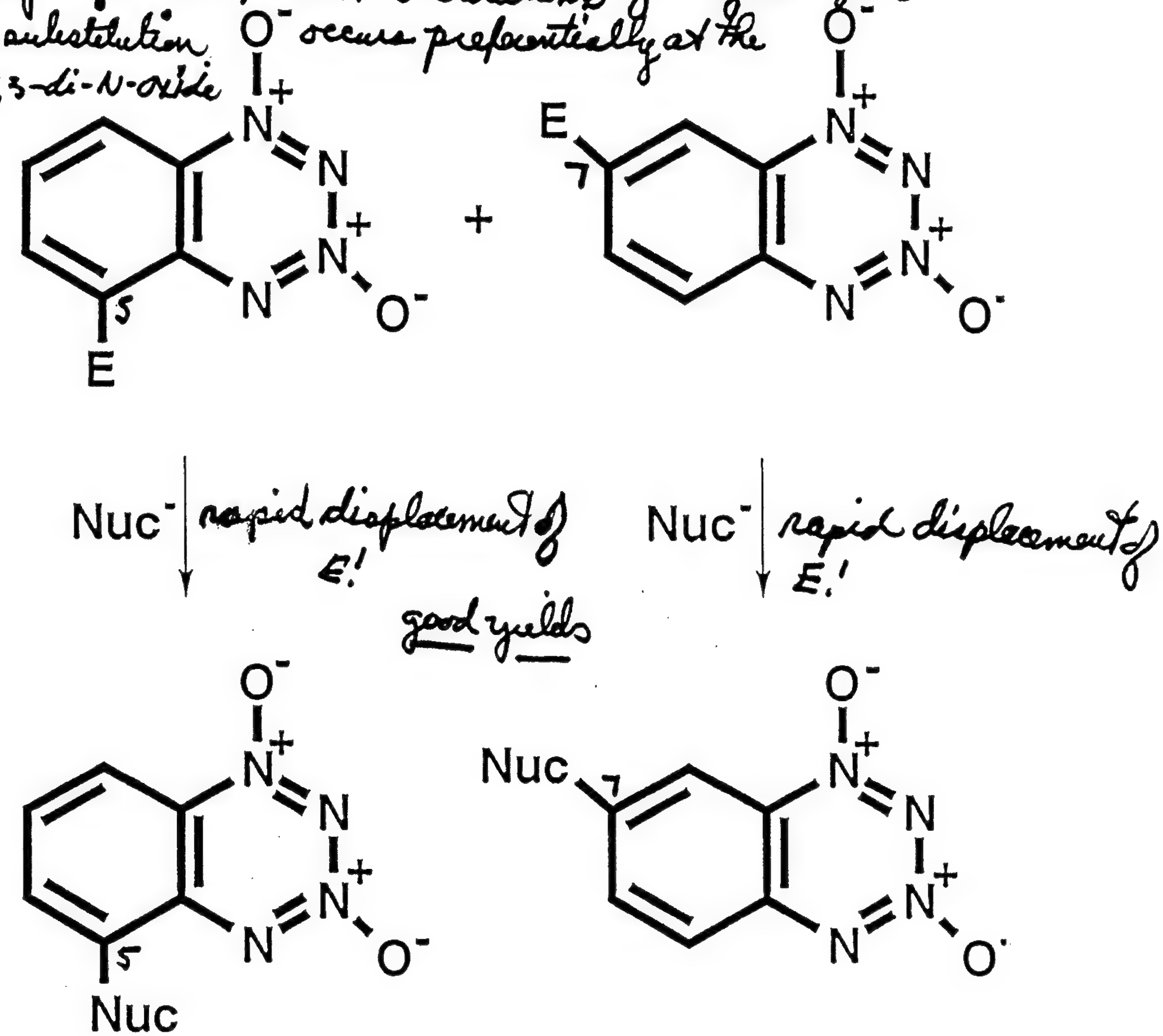
OHIO STATE

A good method developed by Dr. Venugopal for preparing benzotetrazine 1,3-Di-N-oxide.

Substituted Benzotetrazine 1,3-di-N-oxides

Moscow has studied in depth, electrophilic substitutions of Benzotetrazine 1,3-di-N-oxides. Electrophilic substitution occurs preferentially at the 5 and 7 positions. the tetrazine 1,3-di-N-oxide ring stays intact!





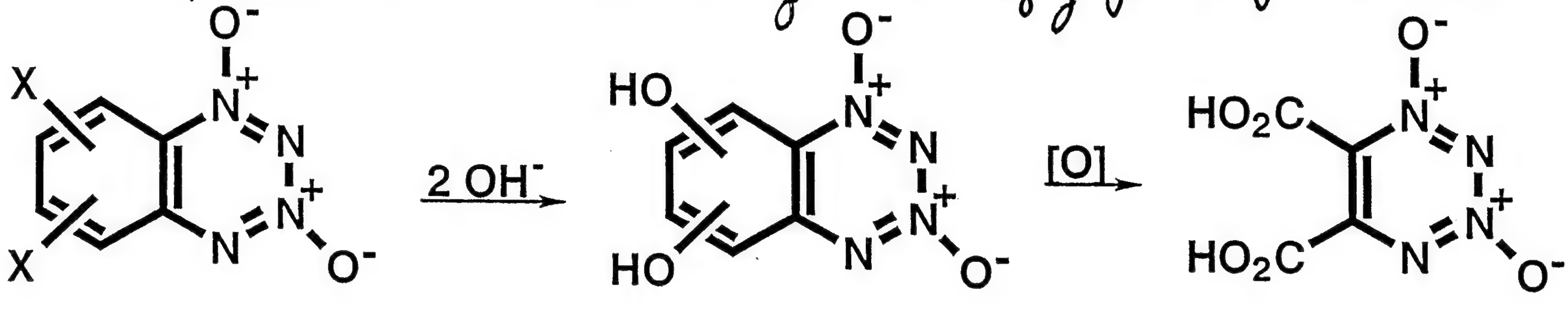
The C_5 and the C_7 substituted benzotetrazines undergo accelerated displacement by various nucleophiles. The behavior of halobenzotetrazine 1,3-di-N-oxides are similar to that of picryl Bromide and 1-fluoro-2,4-dinitrobenzene.

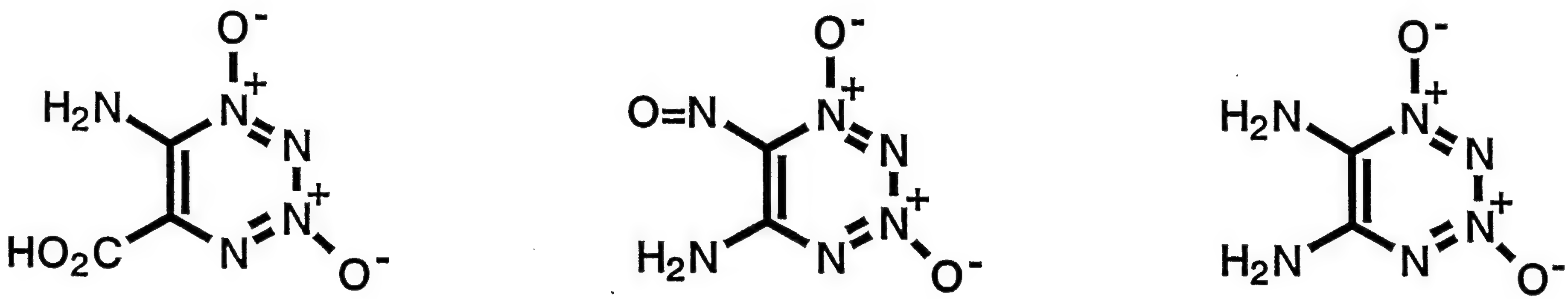
$$E^+ = X^+,\ NO_2^+,\ SO_3;\ Nuc^- = RO^-,\ RS^-,\ R_2NH,\ \text{etc.}$$

Nuc^- = ^-OH, ^-OAc, $^-OSiR_3$, and $^-NH_2$ as displacement nucleophiles have not been reported by Moscow!

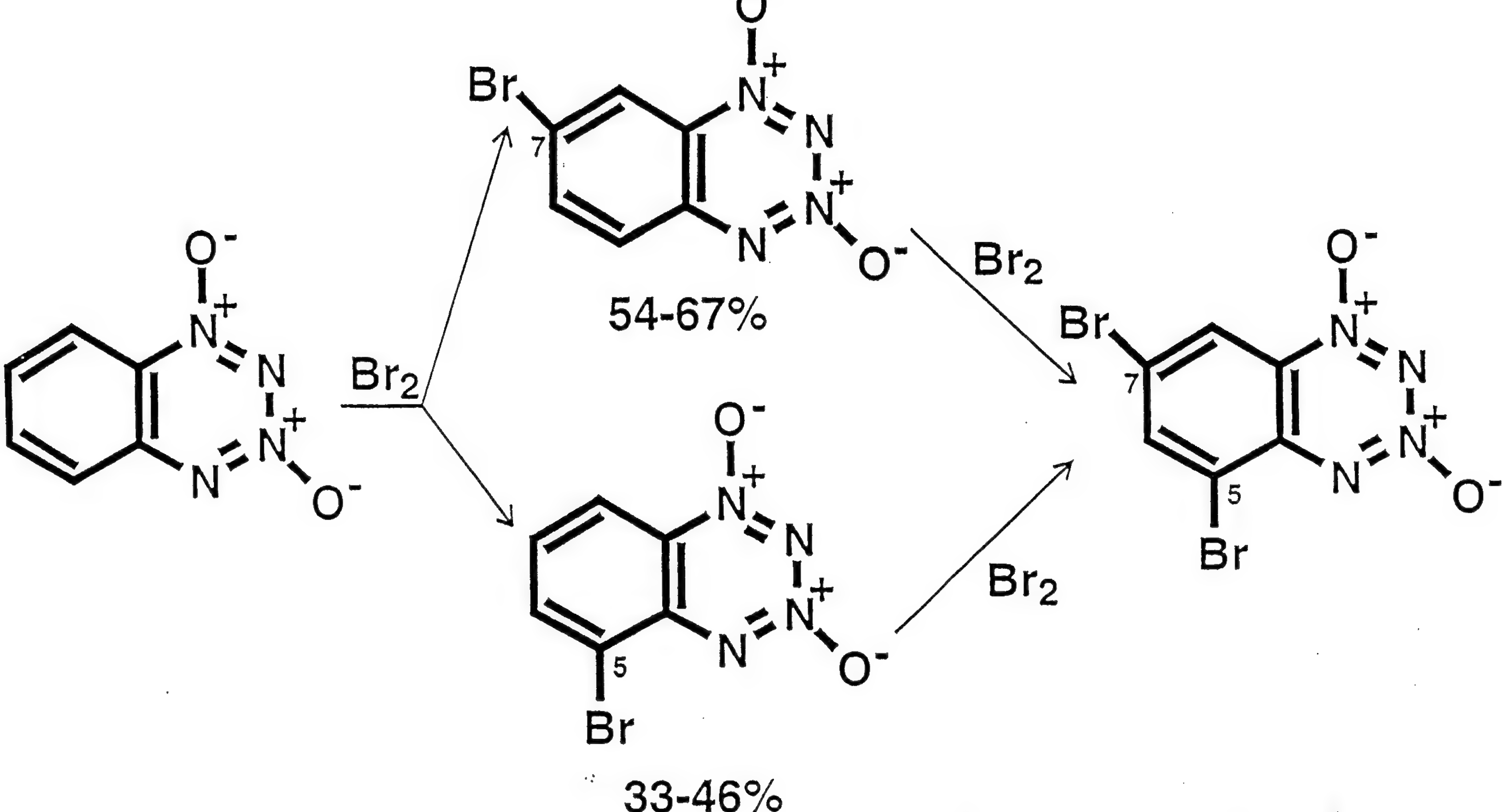
Synthesis of 1,2,3,4-Tetrazine-1,3-di-N-oxides

The following displacements and subsequent reactions are principal present objectives at Iscl at present. Many different oxidizing agents might have to be studied

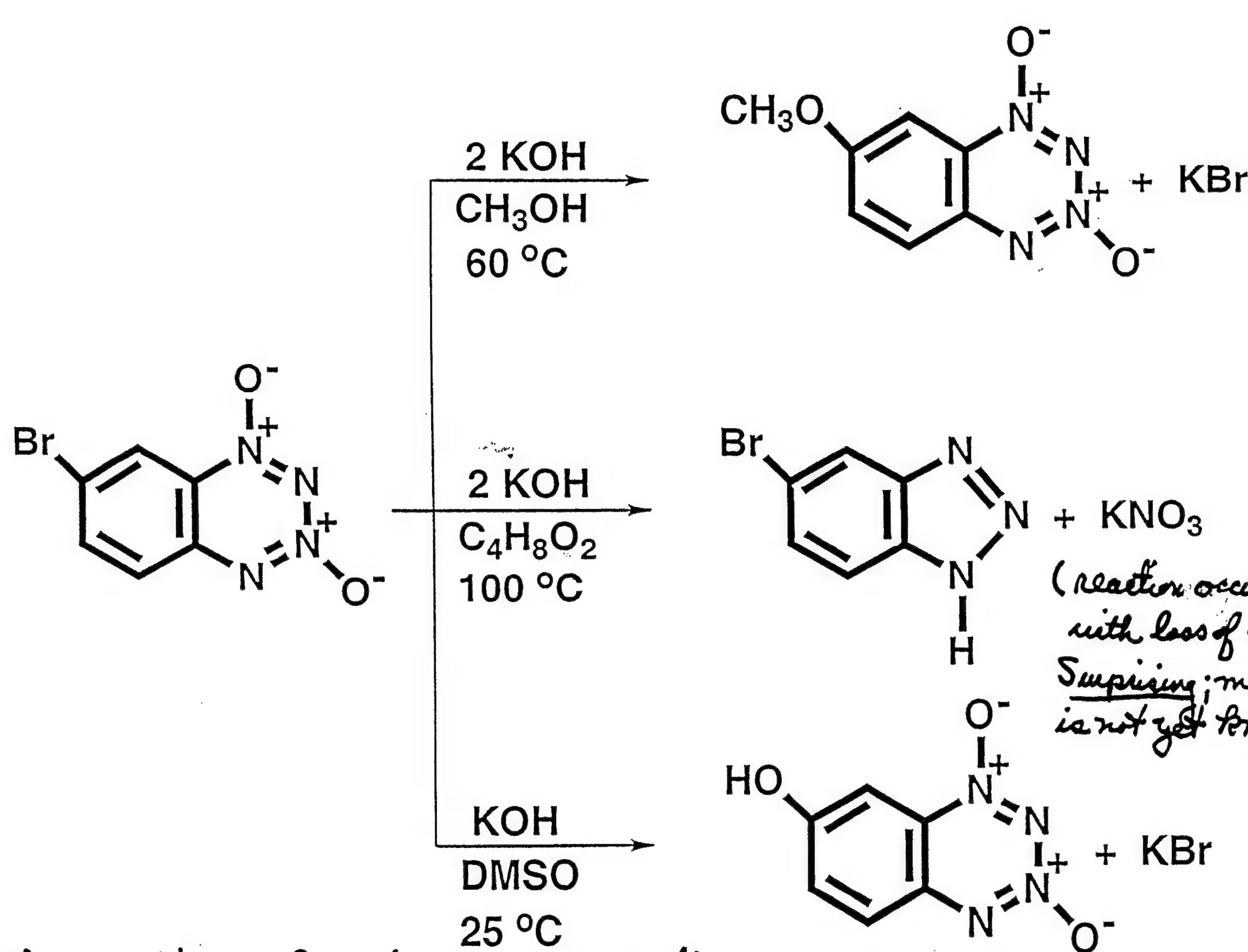




Can mono-1,2,3,4-tetrazine-1,3-di-N-oxides be prepared? Are they sufficiently stable for subsequent use for synthesis of DTTO and/or IsoDTTO? The fundamental physical-organic chemistries of such materials need determination.

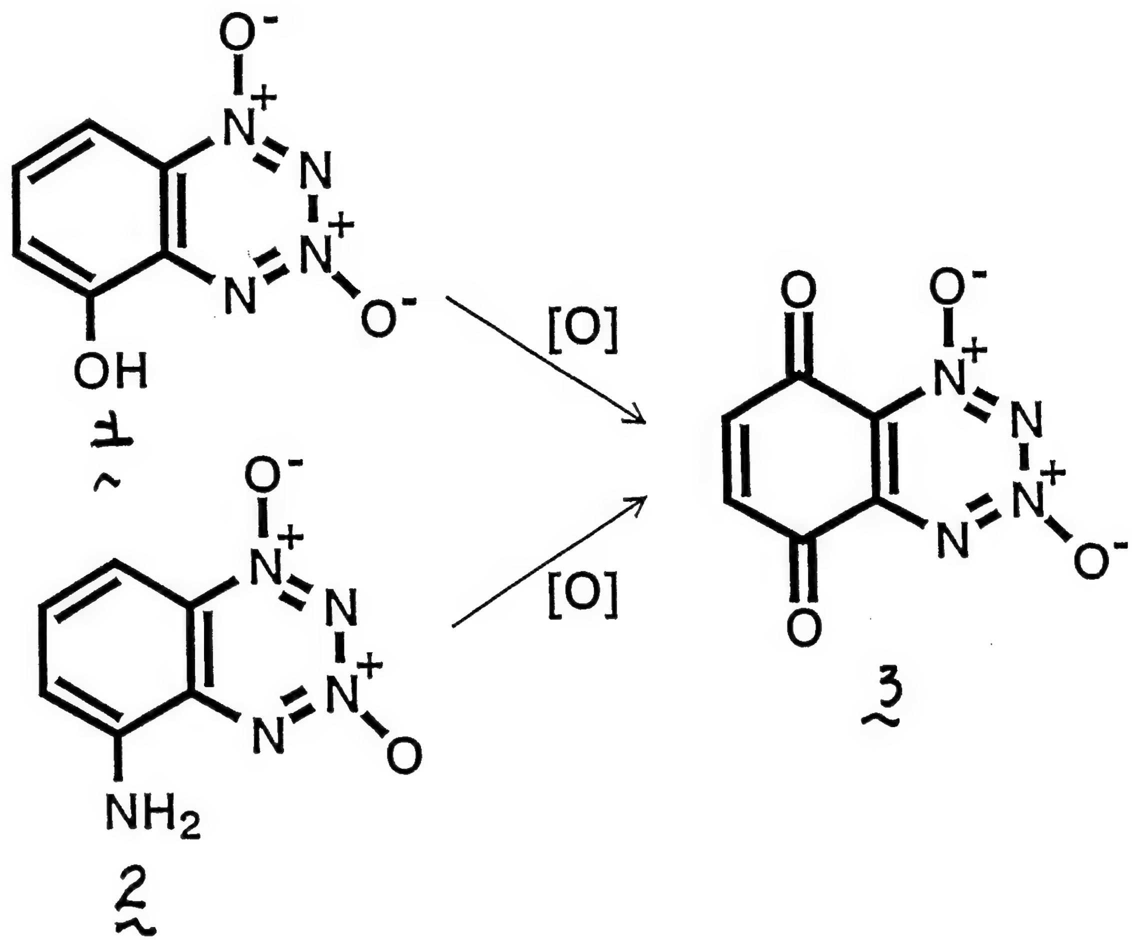


These reactions have been studied at OSU. They work well and the products are readily separated and quite stable. Present results agree with that communicated by Moscow!

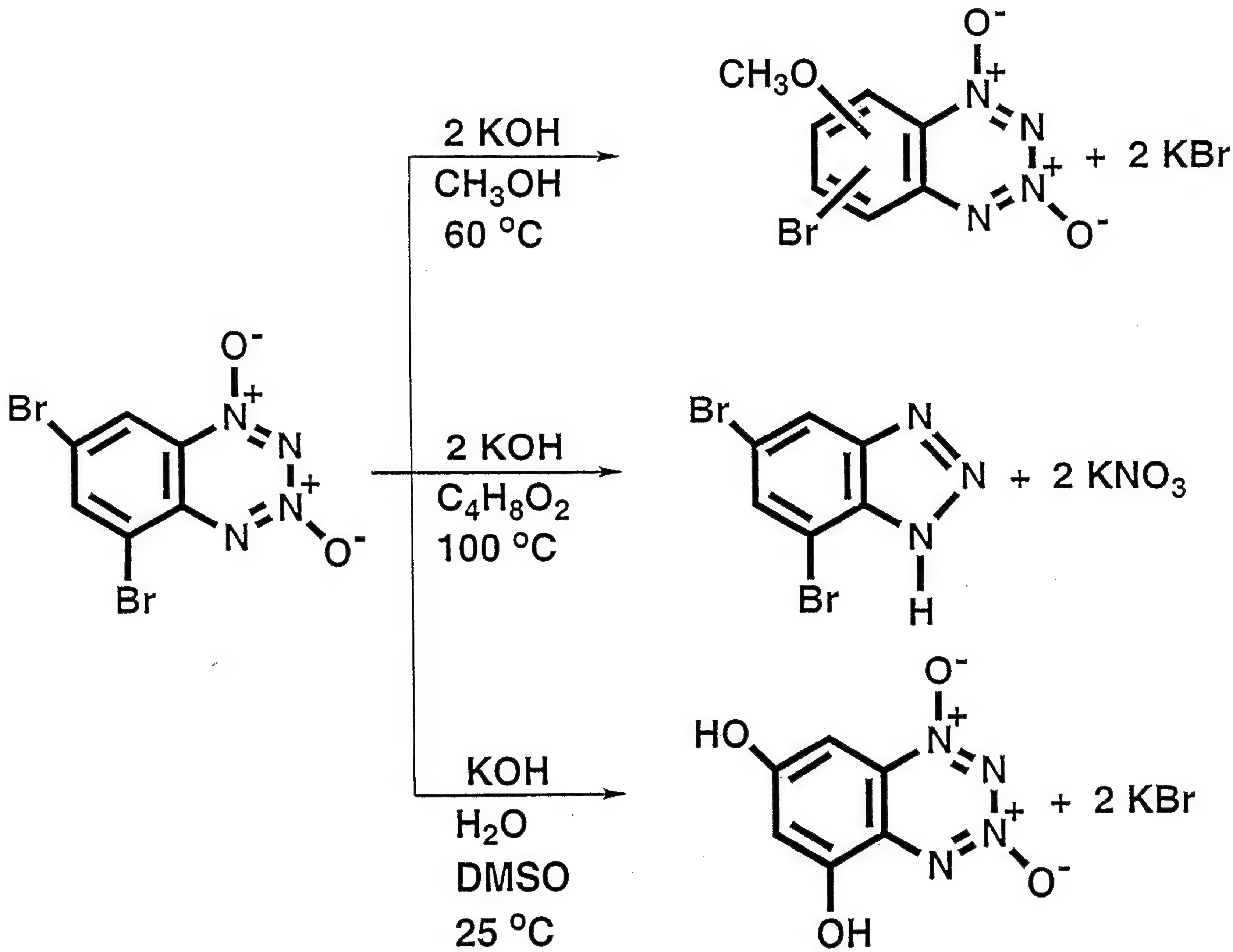


(reaction occurs with loss of NO_2.) Surprising; mechanism is not yet known!

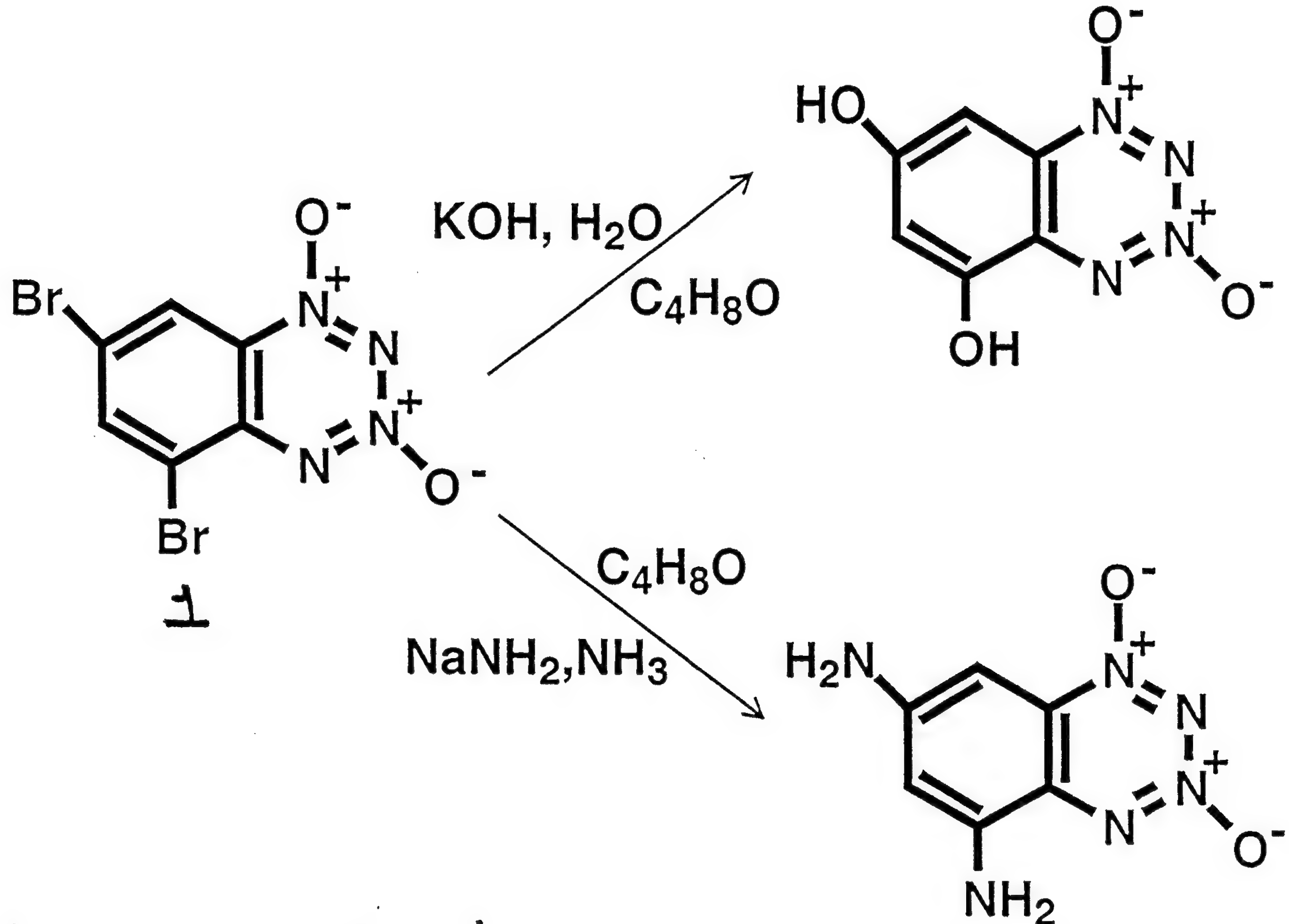
These reactions are being studied at OSU. Reaction 1 occurs as expected. Reaction 2 using KOH at 100°C occurs surprisingly to give the indicated triazole. Reaction 3 at 25°C occurs well. This low temperature reaction will be studied further.



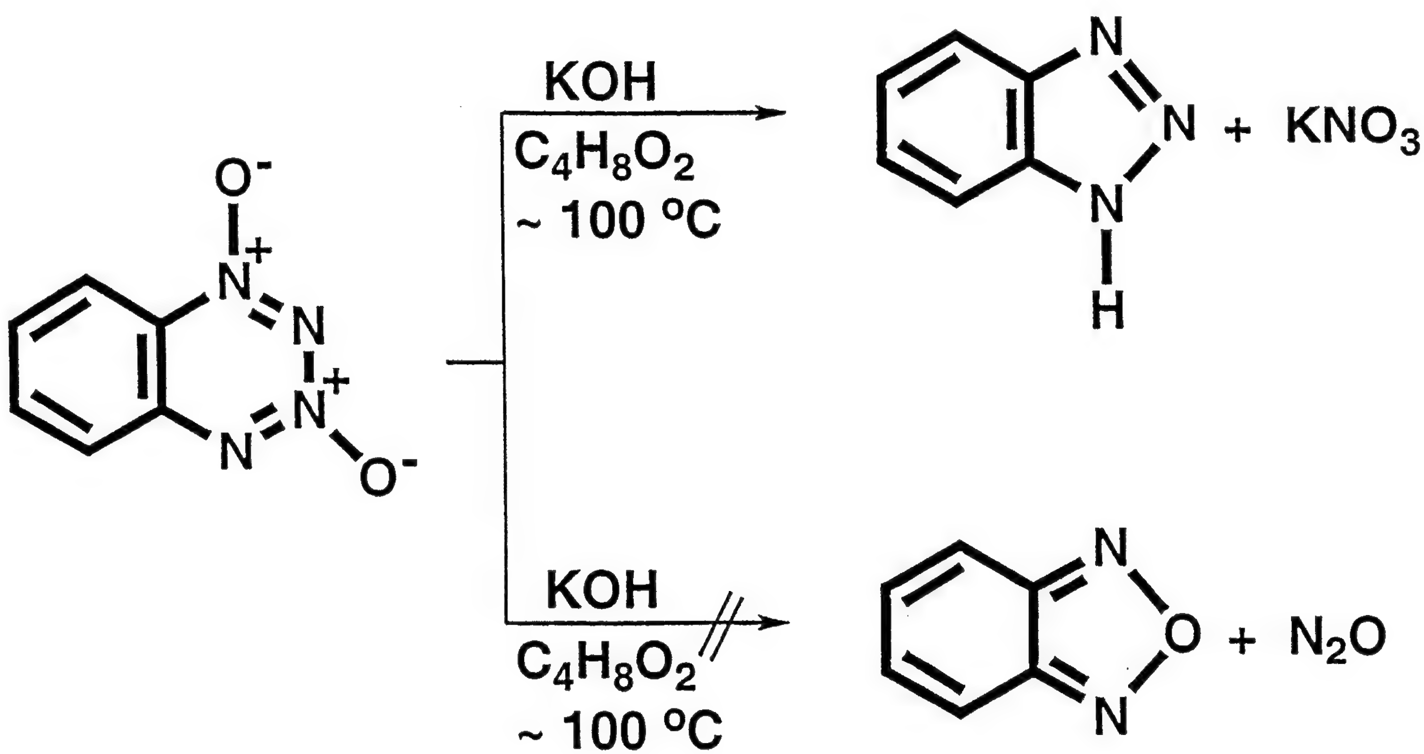
Syntheses of 1 and/or 2 are now being studied. Oxidations of 1 and 2 to quinone 3 or otherwise are to be investigated. Will the 1,2,3,4-tetrazine-1,3-di-N-oxide ring system stay intact?



Br
Br
O-
N+
N
N+
N
O-
2 KOH
CH3OH
60 °C
2 KOH
C4H8O2
100 °C
KOH
H2O
DMSO
25 °C
CH3O
Br
+ 2 KBr
+ 2 KNO3
H
HO
OH
+ 2 KBr

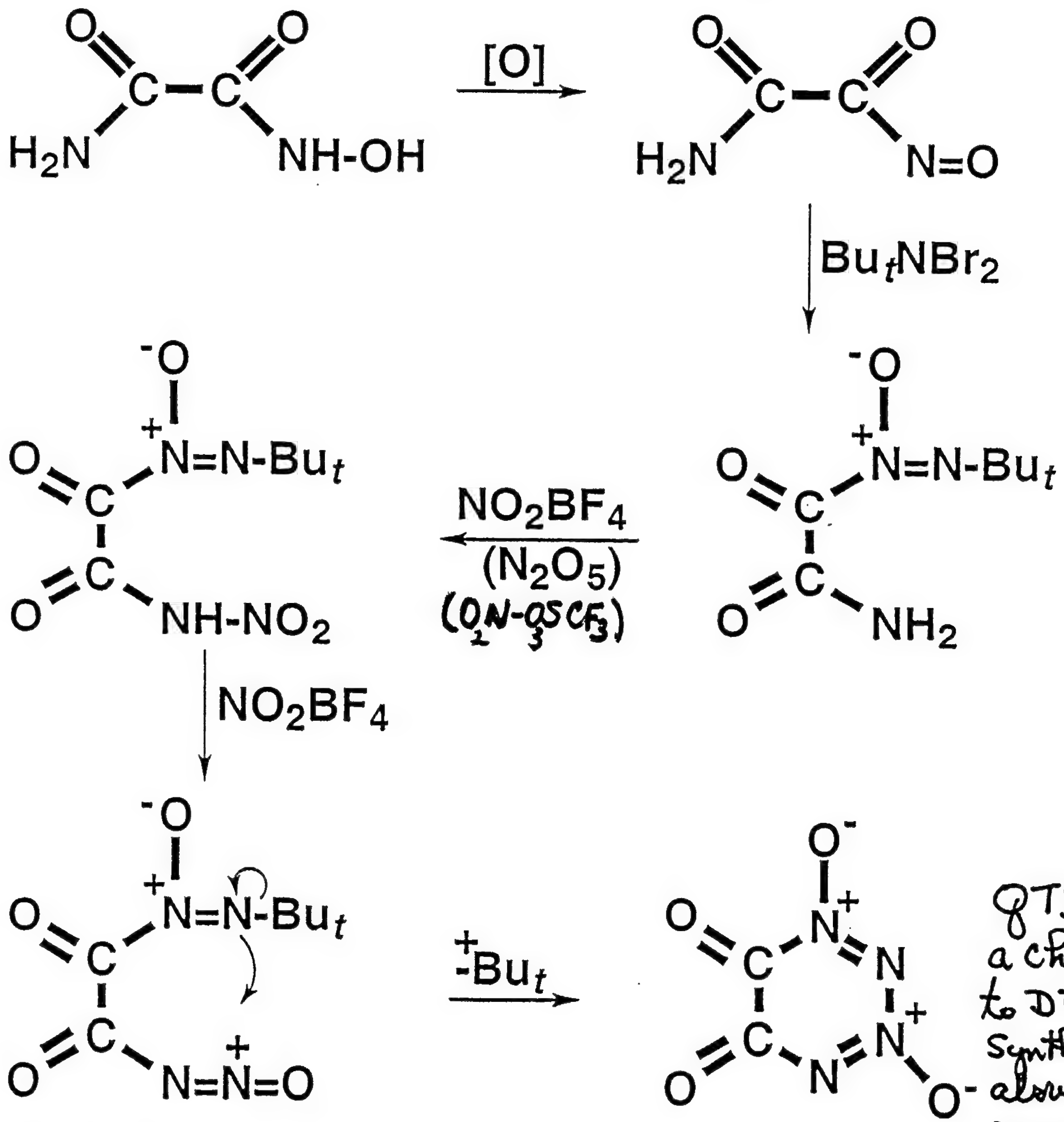


The low temperature behavior of 1 with ^{-}OH and with $^{-}NH_2$ are being studied at OSU at present. The products indicated are to be oxidized in efforts to prepare 1,2,3,4-tetrazine-1,3-di-N-oxide derivatives, usable for preparation of DTTO and/or IsoDTTO.



Reaction of benzotetrazine-1,3-di-N-oxide with hot KOH to give benzotriazole with expulsion of KNO_3 is unexpected. The effects of temperature on the above system are to be determined.

o-Quino-1,2,3,4-tetrazine 1,3-Dioxide (QTDO)

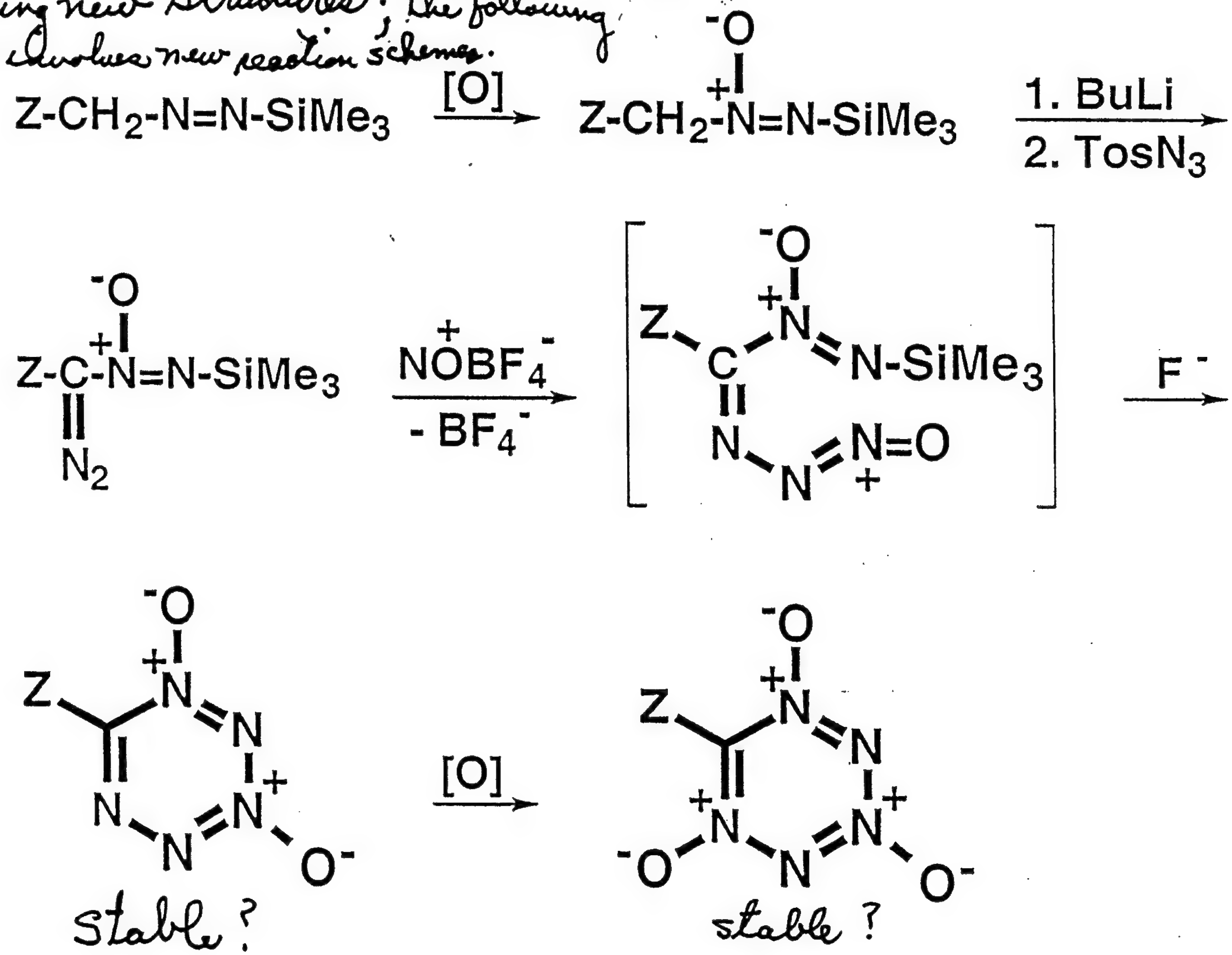


QTDO may be a cheap precursor to DTTO or/and iso DTTO. Synthesis of QTDO as above has been proposed to DARPA/Air Force

QTDO is of interest as an energetic material and, in gasolines etc, as a practical source of N_2O.

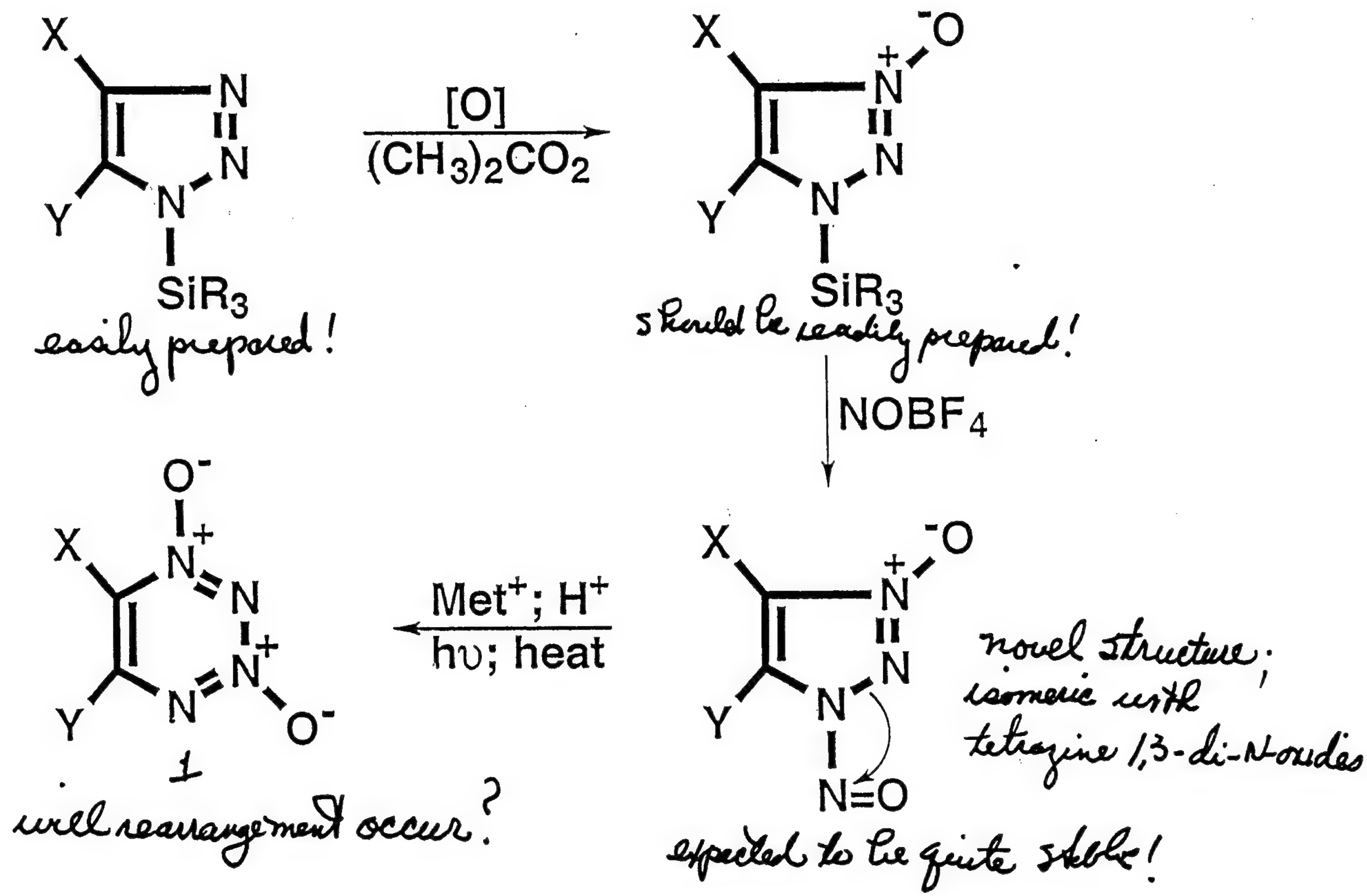
Possible Synthesis of Pentazine N-Oxides

Pentazine N-oxides are unknown; α-diazo-oxides should be stable, highly interesting new structures; the following sequence involves new reaction schemes.



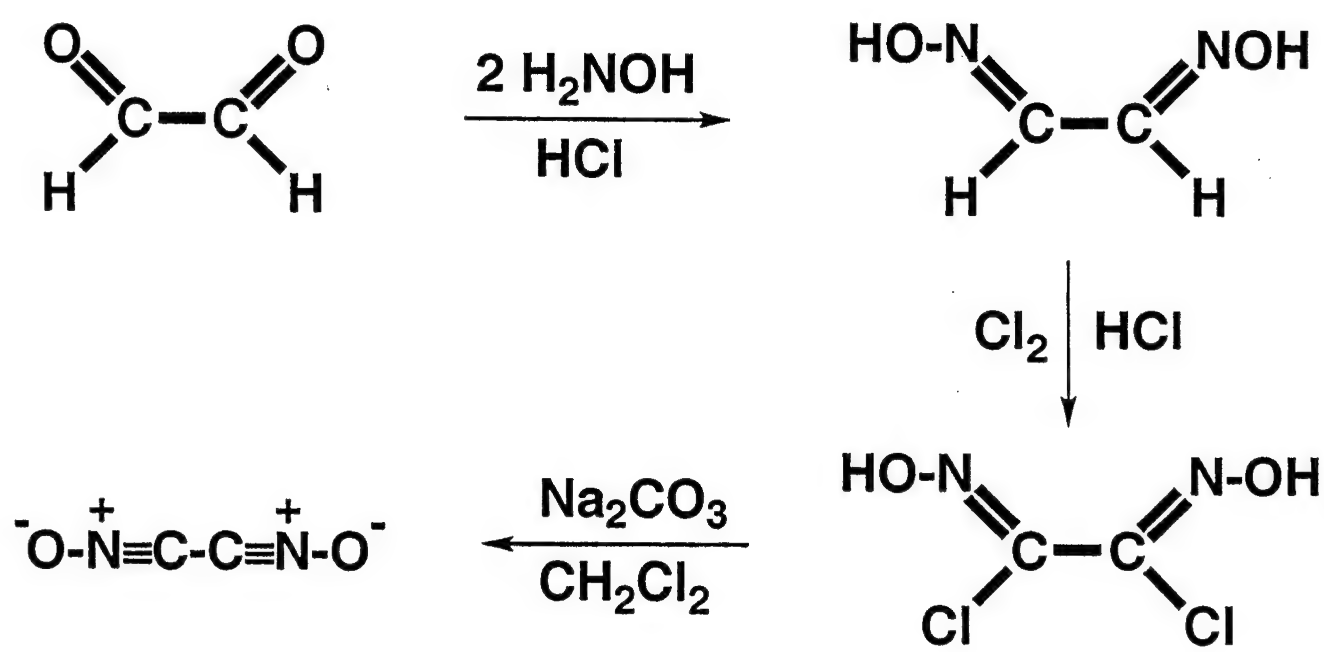
$Z = H, R, Ar, NO_2, CN, RO, X$, etc.

Proposed Synthesis of Tetrazine 1,3-Di-N-oxides



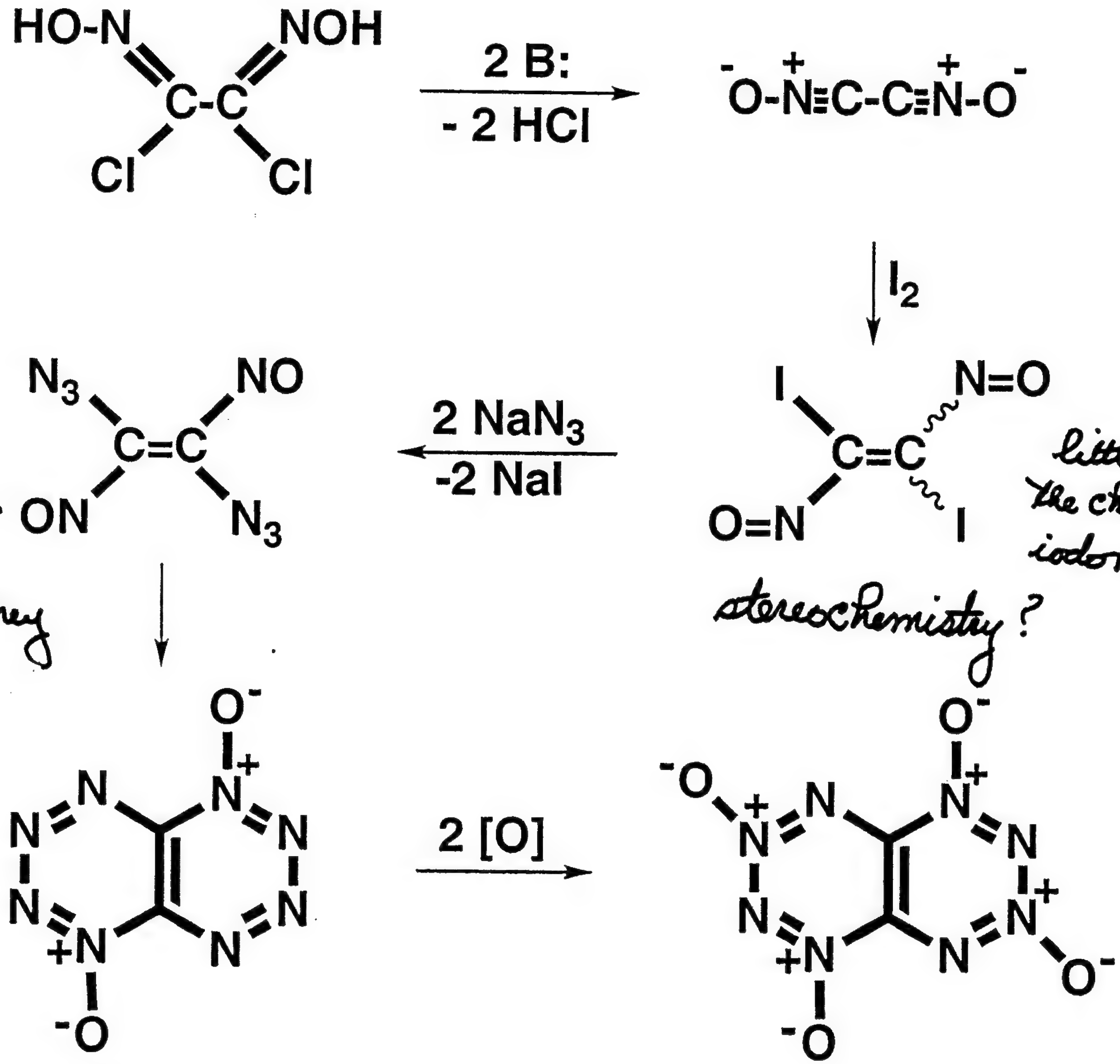
Vary X, Y, R_3Si and Oxidant

Synthesis of Cyanogen N,N′-dioxide



Major programs involving cyanogen N,N-dioxide for synthesis of energetic materials may be envisaged.

Synthesis of IsoDITTO



nothing is known of the behavior of cis-azidonitroso olefins.

Do they cycl

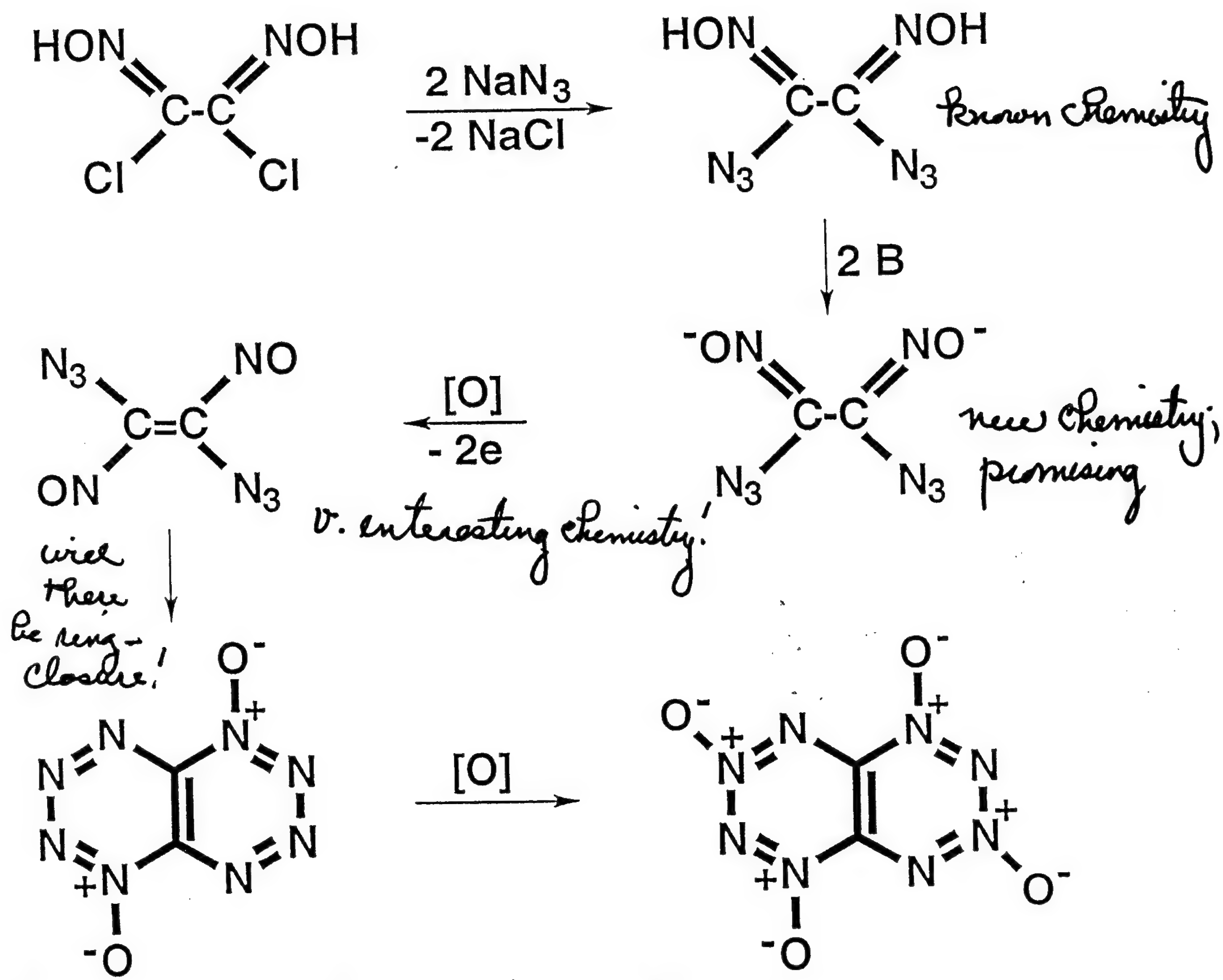
little is known of the chemistry of cis-iodonitroso compounds!

stereochemistry?

Stability?

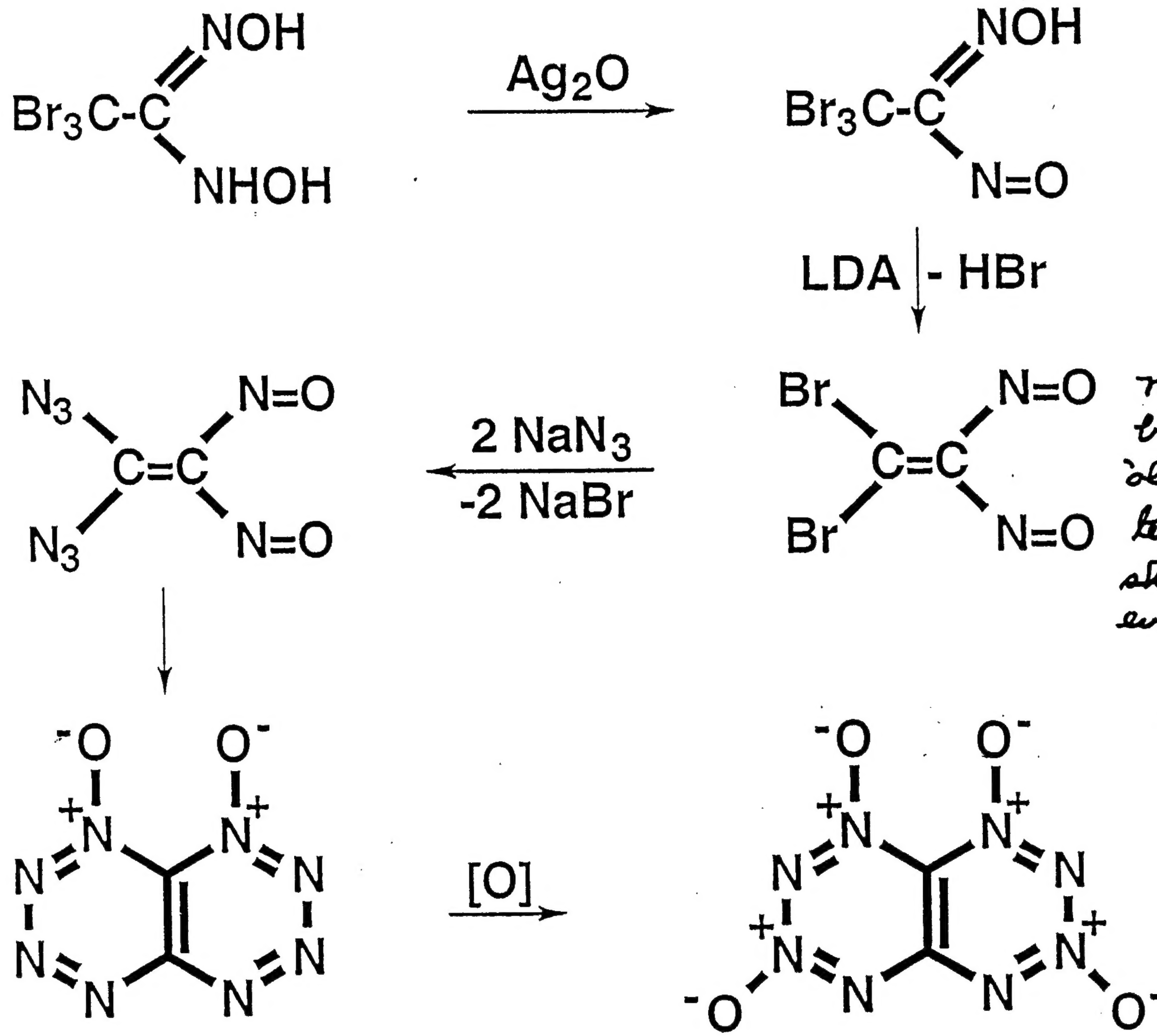
The oxidizing agent will have to be selective.

Possible Synthesis of IsoDTTO



This synthesis of IsoDTTO has not been investigated as yet.
If successful IsoDTTO will be inexpensive!

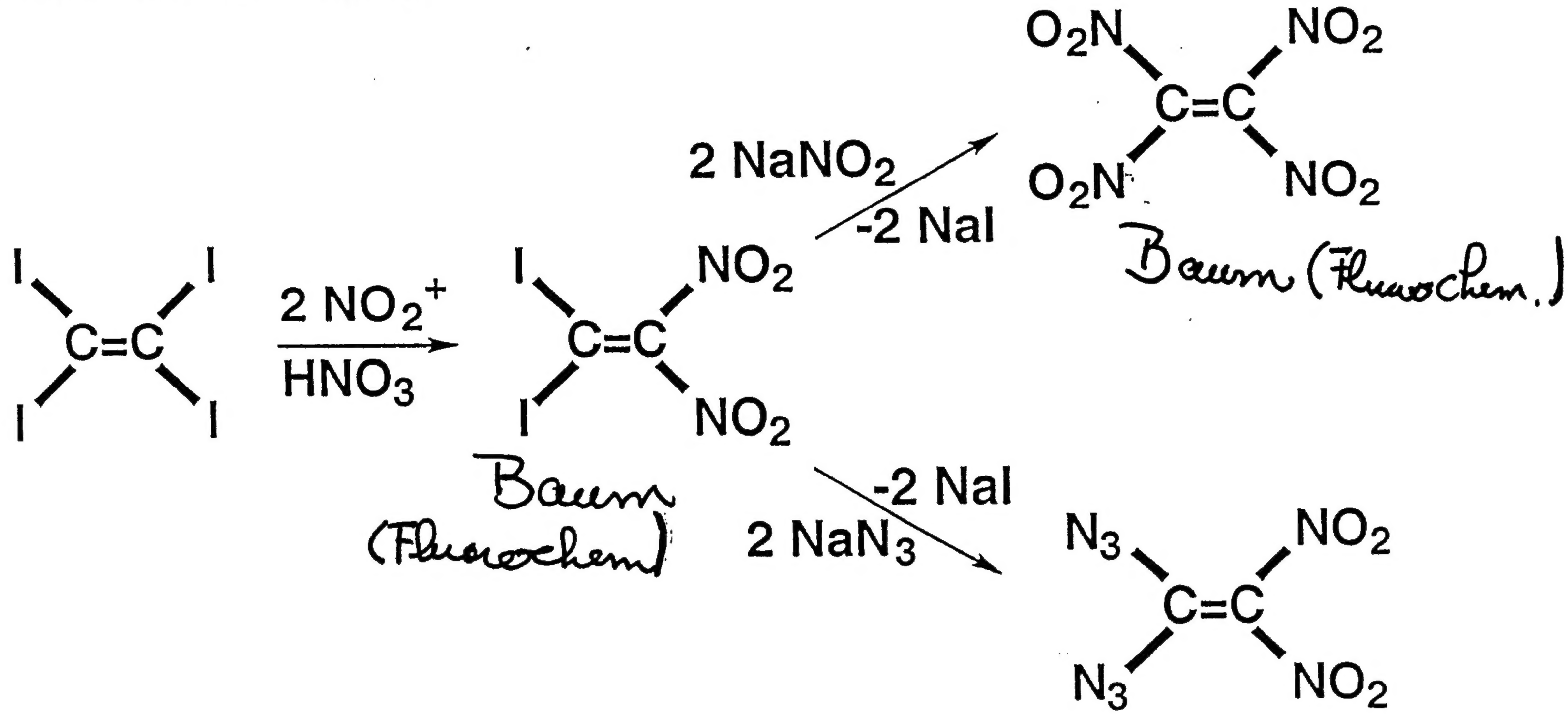
Possible Synthesis of DTTO



Again, do cis-azidoazides ring close to tetrazine-mono-N-oxides?

major programs based on 1,1-dinitroso olefins and tetranitrosoethylene should be carefully evaluated!

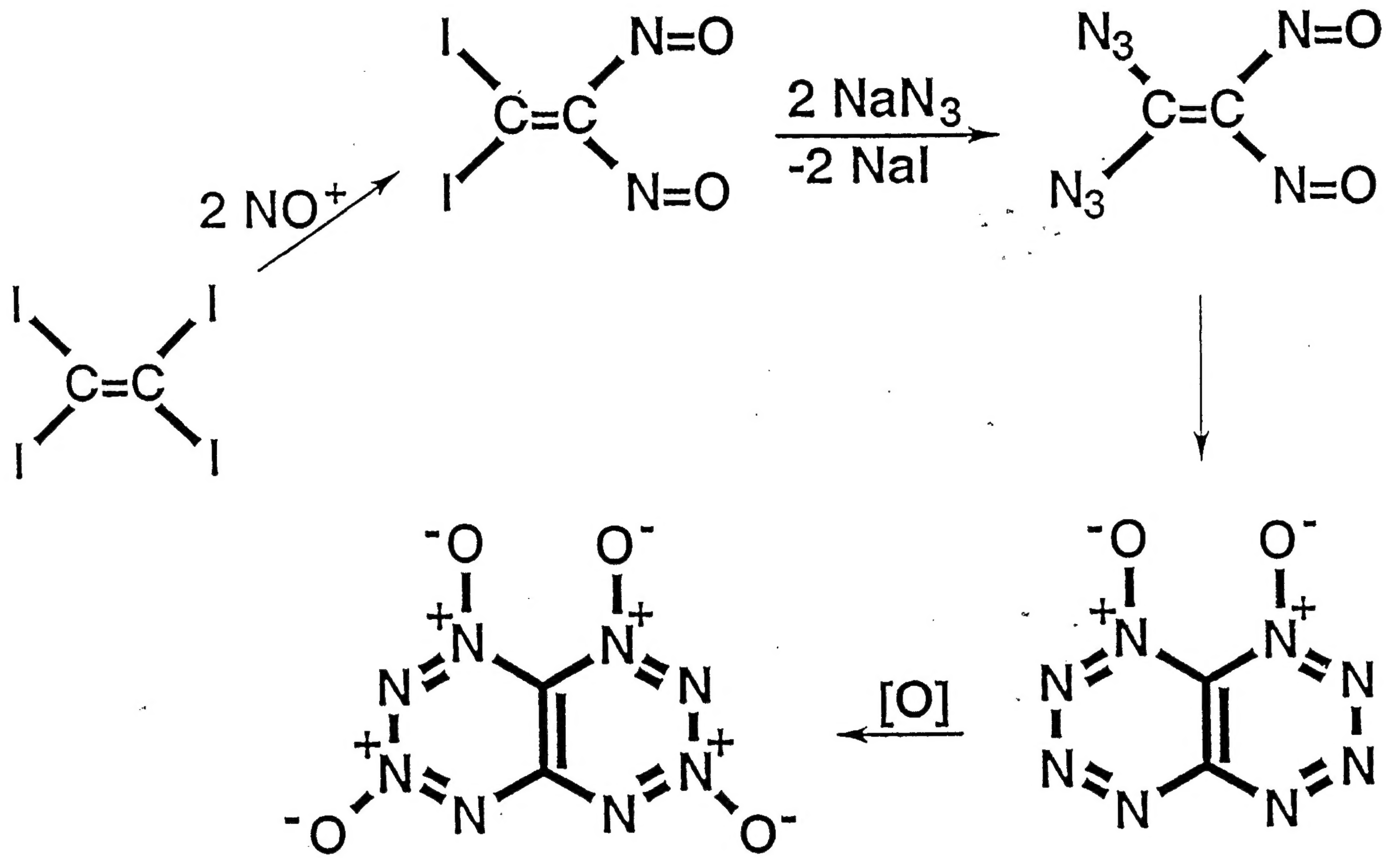
This sequence was developed by Baum at Fluorochem and by Alekseeva at OSU.



Alekseeva (OSU)
A very interesting molecule prepared here which has not been studied further.

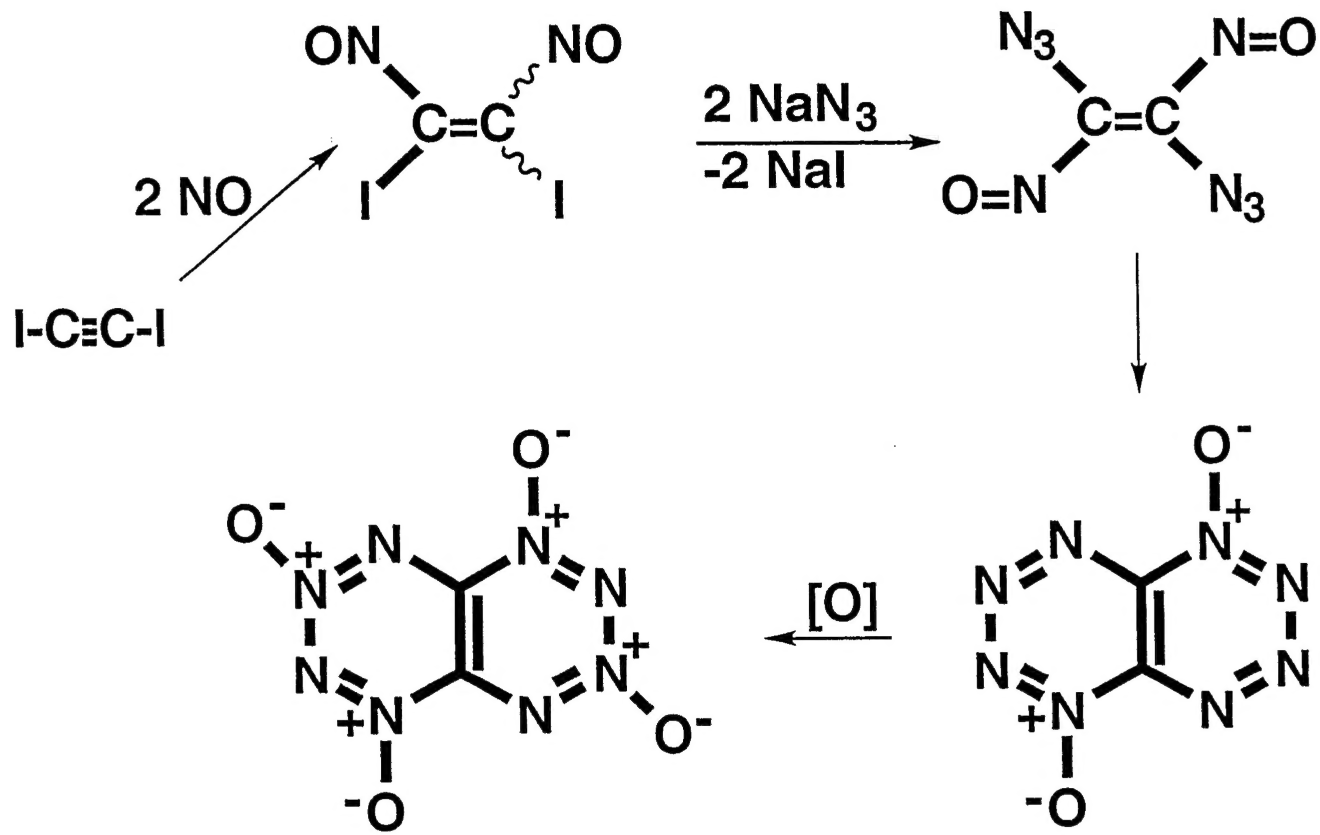
Baum; Alekseeva

Possible Synthesis of DTTO



Major programs on use of tetraiodoethylene, triiodoethylene, and diiodoacetylene should be evaluated.

Possible Synthesis of IsoDTTO



Reactions of diiodoacetylene and N_2O_4 (and other nitrating agents) are being studied on a DARPA program at Ohio State.